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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
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TECHNICAL PROGRESS REVIEWS

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Reactor Fuel Processing Stephen Lawroski and associates
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Reactor Fuel Processing is a Technical Progress Review prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published in this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, G. Bennett, L. Burris, Jr., P. Fineman, A. A. Jonke, G. Kesser, S. Lawroski, W. J. Mecham, P. Nelson, D. Paige, J. Royal, J. Simmons, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

By W. J. Mecham and A. A. Jonke

Fuel-Processing Plans

Processing Plans for Spent Fuel from French Research Reactors

The processing at Savannah River of spent fuel from French research reactors has been arranged by a contract between the U. S. Atomic Energy Commission (AEC) and France's Commissariat a l'Énergie Atomique (CEA). A total of about 1000 kg of aluminum-clad fuel is involved. The fuel is of two enrichments, 20 and 90%. The AEC supplied the uranium under its bilateral agreement with France.

Other negotiations now pending between the interested parties have the intent that other spent fuel, of 90% enrichment, and supplied to France under the U. S.–Euratom agreement, is to be processed at Britain's Dounreay Plant.[1]

Eurochemic Processing Contracts

The Eurochemic fuel-reprocessing plant, now nearing completion, has contracts to recover fuel from the first fuel loading of the 10.7-Mw(e) Belgian Reactor No. 3 (BR-3) and some experimental fuel from France's EDF-1. The BR-3 fuel is about 4% enriched stainless-clad fuel, and the EDF-1 fuel is slightly depleted uranium metal clad in magnesium alloy. Eurochemic has already signed contracts to process fuel from French EL-1, EL-2, and EL-3 research reactors.[2]

Euratom Purchases Plutonium

The AEC has signed a contract for sale of plutonium to Euratom. The total amount covered by the contract is 414.5 kg; part of it is to be supplied as metal and part as oxide. Most of it will be used to fuel fast critical assemblies at the Cadarache Center of France's Commissariat à l'Énergie Atomique and at Germany's Karlsruhe laboratories. The sale does not include plutonium for the second core of the CEA's Rapsodie experimental fast reactor, the purchase of which has been deferred by France. The U. K. Atomic Energy Authority (UKAEA) supplied the plutonium for Rapsodie's first core.

The first shipments of plutonium to Euratom will consist of about 20 kg of PuO_2 produced at Hanford. It will be fabricated into fuel by the German firm ALKEM (Alpha-Chemie und-Metallurgie G.m.b.H.), a company set up last year by Dow Chemical International and NUKEM (Nuclear-Chemie und-Metallurgie G.m.b.H.).[2]

AEC Rules on Facility Classification

The AEC has ruled a proposed commercial plant for processing large quantities of highly radioactive isotopes to be a "utilization facility." As such, the plant will be subject to a licensing process similar to that for nuclear reactors.[3]

The plant, to be known as the Fission Product Conversion and Encapsulation Facility (FPCE), is proposed for construction at AEC's Hanford, Wash., site, by Isochem, Inc., a subsidiary of Martin Marietta Co. and the United States Rubber Company. The purpose of the proposed plant is to recover usable radioisotopes from the waste products remaining after the chemical separation of irradiated reactor fuels. A large quantity of this waste material is stored in underground tanks at the Hanford site. The final product of the facility will be solid encapsulated sources of the radioisotopes ^{90}Sr, ^{137}Cs, ^{144}Ce, and ^{147}Pm. The products are intended for commercial use.

As a utilization facility, the FPCE will be licensed under Commission regulation, Part 50, Licensing of Production and Utilization Facil-

ities, rather than Part 30, Licensing of By-Product Material. This means that a construction permit will be required and a public hearing will be held. The license application will be reviewed by AEC's Advisory Committee on Reactor Safeguards (ACRS), and plant operators will be licensed by the AEC. The Commission will extend Price–Anderson indemnity to the licensed facility.[3]

AEC Plans To License Commercial Radioactive Waste Burial on Land at Hanford

The AEC is proposing to license California Nuclear, Inc., Lafayette, Ind., to bury radioactive waste at the government's Hanford site near Richland, Wash.[4]

The site is located in Benton County, Wash., approximately 1 mile from the southwest corner of the area designated as the 200 East Area of AEC's Hanford Works. California Nuclear, Inc., is presently licensed by the Commission to receive, process, repackage, and store radioactive-waste materials at this site.

The Company would bury only solid wastes in packages as received from customers or in packages prepared by the Company. The waste would be put into open trenches that would be backfilled and then marked in such a manner as to identify the contents and size of the trenches.

Commission regulations require that radioactive wastes be buried on land owned by a state government or the federal government because of the necessity for long-term control over the land. The proposed land burial site is located on land owned by the federal government and leased to the state of Washington. California Nuclear, Inc., will operate the burial ground under a sublease from the state of Washington.[4]

Federal Electric Selected To Negotiate Hanford Support Services Contract

The AEC has selected a proposal by Federal Electric Corporation, Paramus, N. J., as a basis for negotiation of a contract to operate support services at AEC's Hanford plant near Richland, Wash.

The support services at Hanford embrace a large number of diverse functions in support of the laboratory, production reactor, fuel fabrication, and chemical separations operations. The functions include maintenance of plant roads and operation and maintenance of plant railroads and buses; telephone system; electric-power transmission, distribution and substation facilities; guard force; fire department; general stores purchasing and warehousing; heavy equipment; contaminated laundry; printing plant; and other services.

It is anticipated that the operation will cost about $15 million annually and will employ approximately 1150 persons.[5]

AEC Review of Nuclear Industry

A review[6] of the nuclear industry is published annually by the Division of Industrial Participation of AEC. The publication for 1964 included AEC plans, projected economic trends, and lists of firms engaged in various aspects of the nuclear industry.

Short Review of AEC Functions

A general information booklet titled The USAEC — What It Is, What It Does, is available from the Division of Technical Information Extension, Atomic Energy Commission, P. O. Box 62, Oak Ridge, Tenn. The new 68-page brochure includes descriptions of AEC programs, maps of AEC installations and of the sites of power reactors, and a brief explanation of the procedures for regulating the non-government uses of atomic energy to assure safety.[7]

Economics of the Fuel Cycle

Values in Spent Fuel from Power Reactors

A survey was made by Rohrmann[7a] of the values of various isotopes in spent fuel from power reactors. It has been customary, of course, to account for the fissionable plutonium values in the reprocessing of spent fuel, and many possible commercial applications for fission products have been reviewed in the AEC quarterly review *Isotopes and Radiation Technology*. In the present survey, however, an attempt is made to consider the value of all potential by-products which in the future may

afford significant credit to the commercial power-reactor operator or fuel owner as well as profit to the fuel processor.

Besides the expanding markets for fission-product isotopes as radiation and heat sources, large new markets have been predicted for reactor-produced, higher isotopes for use as concentrated heat sources. The most notable of these are ^{244}Cm and ^{238}Pu, with half-lives of 17.6 and 90 years, respectively. The importance of these heavy isotopes is expected to increase as they become more available with installation of new reactors and with recycling of fuel to yield higher isotopes. A summary of the value survey for a typical power-reactor fuel is given in Table I-1.

As shown in Table I-1, the total by-product value is about 1.0 mill/kw-hr, a substantial amount of the total fuel-cycle cost. Of the total fuel values, a small fraction is attached to the fission products, and about equal value is assigned to the group of plutonium isotopes and to the group of other heavy isotopes. The value of ^{236}U in the table derives from its role as a target for ^{237}Np which is a target for the end product ^{238}Pu. Discussions of the reactor production and of separations requirements are given in the report. In this cost analysis, neutrons are found to have a value of $2500/g as a "reagent" in the nuclear transformations conducted in the reactor.[7a]

Spent-Fuel Processing Costs for Advanced Converters

A comparative economic evaluation of several advanced converters has been made at Oak Ridge National Laboratory (ORNL).[8] Conceptual reactor designs of 1000-Mw(e) size were made and cost estimates developed for the power plant and for the complete fuel-cycle costs. The conclusions can be seen from the summary of the cost comparison of the reactor concepts given in Table I-2. The fuel-element characteristics and a breakdown of the comparative fuel-cycle costs are given in more detail in Tables I-3 and I-4, respectively. Because of the complexity of this reactor-oriented study, only the highlights of the economics of the fuel cycle will be cited here. The original

Table I-1 ECONOMIC DATA FOR ISOTOPES AND ELEMENTS[7a]

Isotope or element	Future prices, $/g	Estimated production cost, $/g	Net value in fuel, $/g	Approximate g/ton at 25,000 Mwd/ton	Estimated value, $/ton of spent fuel	
^{85}Kr	300	200	100	17	1,700	
^{90}Sr	20	18	2	411	822	
^{99}Tc	10	9	1	628	628	
Rhodium	6	4	2	337	674	
Ruthenium	2	1.50	0.5	1,707	854	Fission products $7,660
Palladium	1.25	1	0.25	976	244	
Xenon	2	1.70	0.30	3,907	1,196	
^{137}Cs	10	9	1	950	950	
^{144}Ce	25	22.50	2.50	241	260*	
^{147}Pm	30	25	5	133	335†	
^{236}U		0	11	3,277	36,070	
^{238}U	6.75/lb	6.75/lb	0	8.9×10^5	0	
^{237}Np	100	80	20	316	6,320	The higher isotopes $104,110
^{241}Am	100	50	50	56	2,800	
^{243}Am	500	50	450	23	3,450‡	
^{242}Cm	300	150	150	87	39,120	
^{244}Cm	1,000	100	900	22	19,800	
^{238}Pu	500	350	150		3,450	
^{239}Pu	11	2	9	5,453	49,100	Plutonium isotopes $99,185
^{240}Pu	7	2	5	1,517	7,585	
^{241}Pu	19	2	17	1,412	24,000	
^{242}Pu	41	2	39	386	15,050	
			Total value:	per short ton	$210,955	
				per pound	105.50	
				per kilogram	232.50	
				per electrical kilowatt-hour	1.055 mills§	

*At 1 year after discharge.
†At 1 year half-life.
‡As ^{238}Pu, value included with plutonium isotopes.
§At 33⅓% efficiency thermal to electrical.

Table I-2 SUMMARY OF RESULTS OF EVALUATION OF 1000-Mw(e) ADVANCED CONVERTERS[8]

	Pressurized-water reactor (PWR)	Spectral-shift-control reactor (SSCR)	Heavy-water reactor, uranium fueled (HWR-U)	Heavy-water reactor, thorium loaded (HWR-Th)	High-temperature gas-cooled reactor (HTGR)	Sodium–graphite reactor (SGR)
Fuel cycle	Uranium	Thorium	Uranium	Thorium	Thorium	Uranium
Initial fissile inventory, kg/Mw(e)	2.1	3.3	0.6	1.4	2.9	1.7
Thirty-year net fissile make-up, kg/Mw(e)	19	12	24	7.7	3.4	17
Plant* capital cost, $/kw(e)	133	125	125	134	117	130
Heavy-water inventory, $/kw(e)		6	27	33		
Fuel-cycle cost,† mills/kw-hr	1.7–1.8	1.6–1.9	1.0–1.2	1.2–1.4	1.3–1.4	1.4–1.5
Power cost, mills/kw-hr	4.3–4.4	4.1–4.4	3.9–4.1	4.4–4.6	3.6–3.7	3.9–4.0

*Reactor and electrical generation plant.
†Cost breakdown is in Table I-4.

Table I-3 FUEL-ELEMENT CHARACTERISTICS OF ADVANCED-CONVERTER REACTORS[8]

Reactor	PWR	SSCR	HWR-U	HWR-Th	HTGR	SGR
Fuel	UO_2	UO_2-ThO_2	UO_2	ThO_2-UO_2	ThC_2-UC_2	UC
Fuel fabrication	Pelletized	Vibratory compaction	Vibratory compaction and swaging	Vibratory compaction and swaging	Coated particles	Cast, 0.50 in. in diameter
Cladding material	Zircaloy-4	Zircaloy-4	Zircaloy-2	Zircaloy-2	Pyrolytic carbon coating	Zircaloy-2
Coolant	H_2O	H_2O-D_2O	D_2O	D_2O	Helium	Sodium

Table I-4 SUMMARY COMPARISON* OF FUEL-CYCLE COST[8]

	PWR	SSCR	HWR-U	HWR-Th	HTGR	SGR
Case	7	B-3	E-1	G-4	AB-5	1A-2
Last-cycle exposure, Mwd/metric ton	21,050	22,600	11,100	28,500	52,300	19,000
Unit fabrication cost, $/kg	53	60	21.9	37.8	115†	37.5
Unit processing cost, $/kg	31.6	37	16.5	40.2	105	38
Fuel-cycle cost breakdown, mills/kw(e)-hr						
Fabrication	0.34	0.28	0.31	0.22	0.26	0.20
Burnup and losses	0.99	0.70	0.81	0.41	0.20	0.97
Processing	0.20	0.17	0.23	0.24	0.19	0.19
Shipping	0.03	0.03	0.03	0.04	0.05	0.02
Inventory	0.24	0.63	0.10	0.39	0.51	0.27
Interest on fabrication	0.08	0.08	0.04	0.05	0.17	0.03
Interest on processing	−0.01	−0.01	−0.01	−0.01	−0.03	−0.01
Plutonium credit	−0.20		−0.32			−0.14
Total	1.67	1.88	1.19	1.34	1.35	1.53
Estimated range	1.7 to 1.8	1.6 to 1.9	1.0 to 1.2	1.2 to 1.4	1.3 to 1.4	1.4 to 1.5

*Based on 22% per year fixed charges on fabrication and processing plants, 10% per year fixed charges on fuel and fuel-element-fabrication working capital, $7 per gram of fissile plutonium and highly irradiated discharged uranium, $8 per pound of U_3O_8; cost breakdowns based on ORNL 30-year-life physics calculations.
†For recycle of BeO.

report should be consulted for a detailed account of the aims, methods, and significance of the reactor designs and evaluations.

The spent-fuel-processing costs were based on processing the output of fifteen 1000-Mw(e) reactors. The AEC reference plant (1957) and the Nuclear Fuel Services (NFS) plant (soon to be put into operation commercially) were considered as possible cost cases but were rejected. This decision was based on the fact that these two chemical plants (with nominal throughputs of 1000 kg/day) were small for the assumed total plant load and lacked processing facilities for some of the reference fuels. The

alternative course chosen was to adopt a reference design for a single, large, special-purpose, hypothetical aqueous processing plant for each of the reference fuel loads. For comparison with the reference processing plant (costs in Table I-4), typical charges of the AEC and NFS plants were cited as follows: (1) In 1965, the "escalated" daily charges of the AEC plant would be $19,800, with typical unit charges of $24,000 to $39,000 per metric ton. (2) The equivalent NFS charges were calculated to be $31,300 per metric ton (including *minimum* turnaround time). For 3% enriched fuel irradiated to 20,000 Mwd/metric ton at a thermal efficiency of 31%, this corresponds to a minimum processing-cost contribution to nuclear power of about 0.21 mill/kw(e)-hr, with typical costs higher, as follows:

Southern California Edison Co.	0.31 mill/kw(e)-hr
Indian Point UO_2	0.36 mill/kw(e)-hr
Indian Point ThO_2	0.75 mill/kw(e)-hr

The basis for the hypothetical processing plant of the present study was the Du Pont cost study by Farrow,[9] which was a remotely maintained plant of 10 tons/day capacity with a reduced-size version of 1 ton/day. The Du Pont estimates (1961) were escalated by 12% to reflect 1965 price levels and to provide for the particular converter fuels. Costs not included in the Du Pont study were added to cover land, startup, and ultimate disposal of radioactive wastes.

The processing-plant investment costs of the Du Pont study were considered to have an accuracy of ±20%. For the purposes of the present study, 20% was deducted from the Du Pont-based figures, so that the hypothetical processing plant corresponds to the lower limit of the Du Pont estimate. This reduction was said to bring plant costs closer in line with predictions made for the NFS-plant investment costs, although it was considered that the NFS investment prediction may be low.[8]

Fixed charge rates of 15, 22, and 30% were considered for calculating annual capital charges from total capital investment for a privately owned processing plant. The 15% figure corresponds to the privately owned utility financing usually assumed in reactor cost calculations. (The NFS price schedule also appears to reflect a similar charge rate.) The 30% rate would be typical for a company financed essentially completely with common-stock equity capital; however, the high capital-to-operating cost ratio of a radiochemical plant is not consistent with this position, and such a high rate is not likely to be used in the future. The 22% charge rate was adopted in this study[8] as a compromise. Fuel-inventory charges were taken at 10%/year.

Annual operating costs for the hypothetical processing plant were calculated for the same ratios as operating-to-investment costs (not including land, startup expense, and working capital) as the two sizes of Du Pont plants. A summary of the estimated costs for the reference processing plants is given in Table I-5.

The ultimate waste-disposal scheme (costs given in Table I-5) consisted of the following steps: interim liquid storage in as-evaporated acidic form, calcination to solid in stainless-steel pots, interim on-site storage of pots to reduce heat-generation rate, shipment to final disposal facility, and ultimate storage by burial in a salt mine. Cost estimates of these waste operations were based on a previous ORNL study[10] for a 15,000-Mw(e) system. Application to the present study was made by means of a unit-cost formula: $C = 0.643\ P^{0.6}$, where C is the cost of waste operations in mills per electrical kilowatt-hour and P is annual metric tons of fission products. The computed cost for waste disposal was reduced by 20% to compensate for incomplete optimization. The resulting waste-disposal costs were said to be higher than the NFS estimates for a perpetual-liquid-storage scheme.

Other charges related to processing are included in total fuel-cycle costs but are charged separately. These, shown in Table I-4, are facility and inventory charges for 150-day cooling before processing, fuel losses (1%), and inventory charges for holdup time in processing (taken at 30 days). The products of the processing plant are nitrate solutions; conversion charges on this material were calculated separately.

Shipping costs were based on the general methods of Salmon discussed in a report reviewed below. The application to the present fuel cycles involved the following fuel shipments:

1. Spent fuel of high gamma activity shipped from the reactor to the reprocessing plant

2. Recycled (decontaminated) fuel of moderate gamma activity shipped from the refabrication plant to the reactor

3. Nonrecycled (fresh) fuel of zero gamma activity shipped from the refabrication plant to the reactor

The shipping costs were optimized with respect to cask design, cooling time, cask use factor (80%), and processing-plant schedules (85% use factor).

Fuel-fabrication costs were developed in terms of unit costs (dollars per kilogram of heavy metal) for the specific fuel-element designs. Earlier cost estimates of fabrication were used as sources of basic data. The fabrication costs are sensitive to (1) the diameter of the fuel rods, (2) the amount of fuel per unit volume of loaded fuel tube, (3) the number of fuel geometries in a reactor, (4) the number of enrichments, and (5) the fuel enrichment itself, because the capacity of the equipment may be limited by sufficiently high enrichment.

Reactor-irradiated fuel contains radioactive heavy elements as well as fission products. Even after the fission products are removed from the fuel, enough radiation remains to require remote fabrication of the recycle fuel in these advanced converter designs. (A discussion of the radiation hazards for both uranium–thorium and uranium–plutonium recycle fuels was given in the Summer 1964 issue of *Nuclear Safety*.[11])

A summary of fabrication costs is given in Tables I-6 and I-7 for nonrecycle and recycle fuel. The recycle plant is remotely operated, and cost penalties for the remote operation range from about $15 to $23 per kilogram of metal for the 2 metric ton/day throughput rate and $8 to $15 per kilogram of metal for the 5 metric ton/day throughput. Relatively small fabrication-cost differences appeared between pelletized and vibratorily compacted fuel.

"Because of the large-size fuel fabrication and processing methods assumed for this study, costs associated with fabrication and processing range only from 28 to 48% of the fuel cycle total costs for the reference cases. An effect of lowering the importance of these costs is to increase the importance of fuel burnup and

Table I-5 SPENT-FUEL-PROCESSING COST ESTIMATES FOR REFERENCE SINGLE-PURPOSE PLANTS[8]

[Basis: 15,000-Mw(e) Total Capacity, 80% Load Factor, 1000 Mw(e) per Reactor; 310 Operating Days per Year (Processing Plus Turnaround Time); HTGR Case is for Separate Recovery of Uranium Particles for Resale]

	PWR	SSCR	HWR-U	HWR-Th	HTGR	SGR
Reference material burnup, Mwd/metric ton	21,248	29,580	12,540	39,600	48,500	16,750
Thermal efficiency, %	31.1	31.2	26.8	26.1	44.4	43.6
Throughput rates, metric tons/year						
Uranium	645	34.9	1,280	13.9	7.14	587
Thorium		426		393	189	
Plutonium	4.11		5.93			3.42
Fission products	14.1	14.0	16.3	16.7	10.0	10.0
Reference material	663	475	1,300	424	206	600
Batches processed per year	19.2	6.91	57.1	42.4	54.0	48.7
Processing days per year	156	255	155	155	155	155
Processing rates						
Reference material, metric tons/day	4.23	1.86	8.40	2.73	1.37	3.87
Plutonium or highly enriched uranium, kg/day	26.3	137	8.26	89.7	217	22.1
Fissile plutonium and uranium, kg/day	44.7	75.8	38.3	39.7	102	73.5
Total capital investment, 10^6 $	58.5	59.3	65.8	61.1	57.9	59.0
Annual operating cost, 10^6 $	5.37	5.47	6.33	5.69	5.30	5.45
Ultimate disposal charge, 10^6 $/year	2.52	2.51	2.75	2.79	2.05	2.05
Cost at 15% fixed charges						
Total, 10^6 $/year	16.7	16.9	19.0	17.6	16.0	16.4
Unit, $/metric ton of reference material	25,200	35,600	14,600	41,500	77,700	27,300
Unit, mills/kw(e)-hr	0.159	0.161	0.181	0.167	0.152	0.156
Cost at 22% fixed charges						
Total, 10^6 $/year	20.8	21.0	23.6	21.9	20.1	20.5
Unit, $/metric ton of reference material	31,400	44,200	18,200	51,700	97,600	34,200
Unit, mills/kw(e)-hr	0.198	0.200	0.224	0.208	0.191	0.195

Table I-6 FABRICATION COSTS FOR NONRECYCLE FUEL IN SINGLE-PURPOSE PLANTS[8]

(Amortization Rate: 22%)

Reactor	Type of fuel element	Fabrication cost ($/kg of heavy metal) based on heavy-metal throughput*					Type of plant
		500*	1000*	3000*	5000*	10,000*	
PWR	Vibratorily compacted	114	71	50	45		Contact
PWR	Pellets	127	85	60	53		Contact
SSCR		106	65	45	40		Hooded
HWR-U			47	27.5	23	18	Contact
HWR-Th			52	28	23.5	18.5	Hooded
HTGR	250-μ particles, virgin BeO	162	145				Hooded
HTGR	250-μ particles, recycle BeO	96	82				Hooded
HTGR	1000-μ particles, virgin BeO	164	148				Hooded
HTGR	1000-μ particles, recycle BeO	100	84				Hooded
SGR	Zirconium-clad, vented	100	64	35	28		Contact
SGR	Stainless-steel-clad, nonvented	96	58	30	23.5		Contact

*Heavy-metal throughput in kilograms per day.

Table I-7 FABRICATION COSTS FOR RECYCLE FUEL IN SINGLE-PURPOSE PLANTS[8]

(Amortization Rate: 22%)

Reactor	Type of fuel element	Fabrication cost ($/kg of heavy metal) based on heavy-metal throughput*					Type of plant
		500*	1000*	3000*	5000*	10,000*	
PWR	Vibratorily compacted	143	92	68	59		Remote
PWR	Pellets	163	108	77	68		Remote
SSCR		132	80	57	50		Remote
HWR-U			54	32	26	20.5	Remote
HWR-Th			58	32.5	26.5	21	Remote
HTGR	250-μ particles, virgin BeO	180	160				Remote
HTGR	250-μ particles, recycle BeO	115	100				Remote
HTGR	1000-μ particles, virgin BeO	183	165				Remote
HTGR	1000-μ particles, recycle BeO	120	102				Remote
SGR	Zirconium-clad, vented	131	82	44	36		Remote
SGR	Stainless-steel-clad, nonvented	127	76	39	31.5		Remote

*Heavy-metal throughput in kilograms per day.

inventory costs, particularly for a 10% inventory charge. Consequently, the fuel cycles generally tend to optimize at lower burnups than those cited for the reference designs by the concept sponsors."[8]

Economic Evaluation of Close-Coupled Fuel Processing

Close-coupled processing facilities have potential advantages, compared to large centrally located facilities, of simplified, special-purpose processing requirements, of reduced ex-reactor inventory charges, and the elimination of shipping charges. An economic evaluation of close-coupled fuel reprocessing has been made by McKee.[12] In this study the reference load for the close-coupled processing plants was taken as 1000 Mw(e), and the associated reactor fueling was taken as representative of light-water reactor types with enrichments in the range 1.4 to 4.5% and fuel exposures in the range 10,000 to 40,000 Mwd/ton. The reactor case descriptions are shown in Table I-8. By assuming several reactors at a single site operating with staggered fuel discharge schedules, fuel was available for reprocessing at three-month intervals. Longer periods of elapsed time between fuel discharges, as might be encountered in a single, batch-fueled reactor, do not allow the close-coupled plant to take advantage of its capability for handling short-cooled fuel. The plutonium generated in the reactor was used for refueling. The study did not at-

Table I-8 REACTOR CASE DESCRIPTIONS[12]

[Net Electric Power 1000 Mw(e); Thermal Efficiency 33%; Plant Factor 80%]

Case	Typical water reactor		Advanced pressurized-water reactor (APWR)
	TWR(I)	TWR(II)	
Cladding material	Stainless steel	Zirconium	Stainless steel
Cladding thickness	0.010 in.	0.020 in.	0.0162 in.
Fuel	UO_2-PuO_2	UO_2-PuO_2	UO_2-PuO_2
Fuel diameter	0.5 in.	0.5 in.	0.375 in.
Fuel density	95% theoretical	95% theoretical	96% theoretical
Fuel-to-moderator ratio	0.483	0.483	0.598
Specific power	15 Mw/ton	15 Mw/ton	20 Mw/ton
Fuel management	Graded cycle with partial core discharge at one-month intervals or at three-month intervals if a three-reactor complex is assumed		Graded cycle with partial core discharge at three-month intervals or at nine-month intervals if a three-reactor complex is assumed

tempt to develop definitive plant cost estimates but made cost comparisons between central and close-coupled plants for the entire fuel cycle, including in-reactor inventory.

Basic unit costs (dollars per kilogram of fuel) were taken from published estimates for hypothetical central processing and fabrication plants and for other components of the fuel cycle. The unit cost estimates were grouped into high- and low-range costs to develop a probable range of fuel-cycle costs. Total fuel-cycle costs for the reference central-plant fuel cycle derived from these unit costs are summarized in Table I-9. When a simple cost model was assumed for operating costs and capital-based charges, the allowable capital investment for close-coupled plants was calculated, relative to the corresponding central-plant fuel-cycle cost, both with and without fuel-cycle cost savings. These results are shown in Table I-10. An analysis was made for the total fuel-cycle cost (mills per electrical kilowatt-hour) as a function of fuel exposure (megawatt-days per ton) with various processing plant unit costs (dollars per kilogram) and equivalent investment costs (dollars) as parameters. The study was specifically related to the application of the salt-cycle process under development at Hanford for close-coupled plutonium-recycle processing with the aim of defining the processing requirements for such processes and determining the magnitude of economic incentives for their application to a range of reactor types.

A cost estimate was made for a close-coupled facility for salt-cycle processing and refabrication of oxide fuel by vibratory compaction. Because the fuel is only partially decontaminated (decontamination factor of 6), the refabrication as well as the processing steps are carried out fully remotely in a circular cell (with an annular operating zone of 4900 sq ft) equipped with shielded windows, manipulators, etc. A schematic diagram of the plant

Table I-9 CENTRAL-PLANT REPROCESSING FUEL-CYCLE COSTS[12]

Reactor case	Economics case	Fuel-cycle cost at 20,000 Mwd/ton, mills/kw(e)-hr	Optimum fuel cycle	
			Exposure, Mwd/ton	Cost, mills/kw(e)-hr
APWR	Low-range and purchase U	1.817	31,000	1.739
	High-range and purchase U	2.085	35,000	1.920
TWR S.S.-clad	Low-range and purchase U	1.468	24,000	1.452
	High-range and purchase U	1.720	28,000	1.653
TWR, zirconium-clad	Low-range and purchase U	1.353	23,000	1.345
	High-range and purchase U	1.703	28,000	1.647

Table I-10 CLOSE-COUPLED-PLANT ALLOWABLE INVESTMENT FOR A 1000-Mw(e) REACTOR COMPLEX[12]

Central-plant fuel exposure, Mwd/ton	Fission-product poison, DF	Fuels-cycle savings, mills/kw(e)-hr	Allowable investment, millions of dollars		
			APWR reactor case	TWR reactor cases	
				S.S.-clad	Zirconium-clad
20,000	∞	0.0	7.3 to 9.9	6.4 to 8.9	6.1 to 7.8
		0.1	5.6 to 8.2	4.5 to 7.1	3.6 to 6.0
	6	0.0	6.8 to 9.4	5.7 to 8.0	4.9 to 6.9
		0.1	5.1 to 7.7	3.8 to 6.4	2.9 to 5.3
Optimum	∞	0.0	6.0 to 7.3	6.1 to 7.7	5.8 to 6.8
		0.1	4.2 to 5.6	4.1 to 6.0	3.3 to 5.0
	6	0.0	5.5 to 6.8	5.3 to 6.9	4.7 to 6.0
		0.1	3.7 to 5.0	3.6 to 5.3	2.7 to 4.4

is shown in Fig. I-1. The cost estimate for this plant was $6.2 million. The remote cell design is similar to that of the existing fuel-cycle facility in Idaho, which serves the 60-Mw(e) [Experimental Breeder Reactor No. 2 (EBR-II)] metal-fueled fast reactor.

The hypothetical $6.2 million plant was used as a reference for making calculations[12] of the amount of net savings of the close-coupled process compared to the central processing plant; these results are summarized in Table I-11. (The annual savings can be found by multiplying the unit cost savings (mills per electrical kilowatt-hour) of Table I-11 by 7.0×10^9 kw(e)-hr/year for the reference 1000-Mw(e) reactor.) It was noted that the savings quoted are over and above normal profits, amortization, taxes, insurance, etc.

The existence of optimum burnups (i.e., minimum fuel-cycle costs at certain burnups) for both central and close-coupled plants follows from the fact that various components of the total fuel cycle (at a fixed reactor power) respond differently to variations in total fuel throughput rate (kilograms per year) corresponding to different burnups. For example, annual charges for fuel inventory and fabrication tend respectively to increase and to decrease with increasing burnup. For the economic data of this study, the central plant optimized at 25,000 to 35,000 Mwd/ton and the close-coupled plant at about half that figure. In terms of processing load, the optimum throughput for the close-coupled separations plant was about 45,000 kg/year. (Although the study was limited to a 1000-Mw(e) close-coupled processing plant, it is clear that a larger plant, say 2000 Mw(e), would be expected to show increased economic advantage over the central processing plant.)

In the study are discussed the important ways in which fuel management schemes can be used to advantage in reducing fuel inventory for close-coupled plants. Also, an assessment made of low-decontamination (DF = 6) separations in the close-coupled plant showed an increase in cost compared to that for a high-decontamination separations process. The penalty for incomplete removal of the fission-product poisons was indicated to be about $0.75 million in allowable plant investment, or 0.04 mill/kw-hr at fixed investment. (At the indicated optimum throughput for the close-coupled plant, this differential would be about $6.2 per kilogram.) The cost penalty for low decontamination has its source in the fabrication of PuO_2-UO_2 fuel elements. Unit costs for direct fabrication portion of the fuel-fabrication costs (i.e., excluding material and inventory costs) were about $20 per kilogram higher for the incomplete removal of fission products compared to complete removal.

It was noted that close-coupled plants can be based on a completely different technology from that used in central-plant processing for which the highly flexible solvent-extraction processes have been developed. In addition, the report cited additional qualitative advantages that might be achieved by close-coupled processes. These include:

a. Increasing public safety through minimized long distance shipment of irradiated fuels and plutonium;

b. Establishing a closed-loop recycle system with improved reactor performance through better technical feedback (burnup analyses, post-irradiation examination, etc.);

c. Providing as part of the basic facility the potential for remote refabrication of fuel to capitalize on technical progress in fuel rejuvenation and cladding reuse techniques.[12]

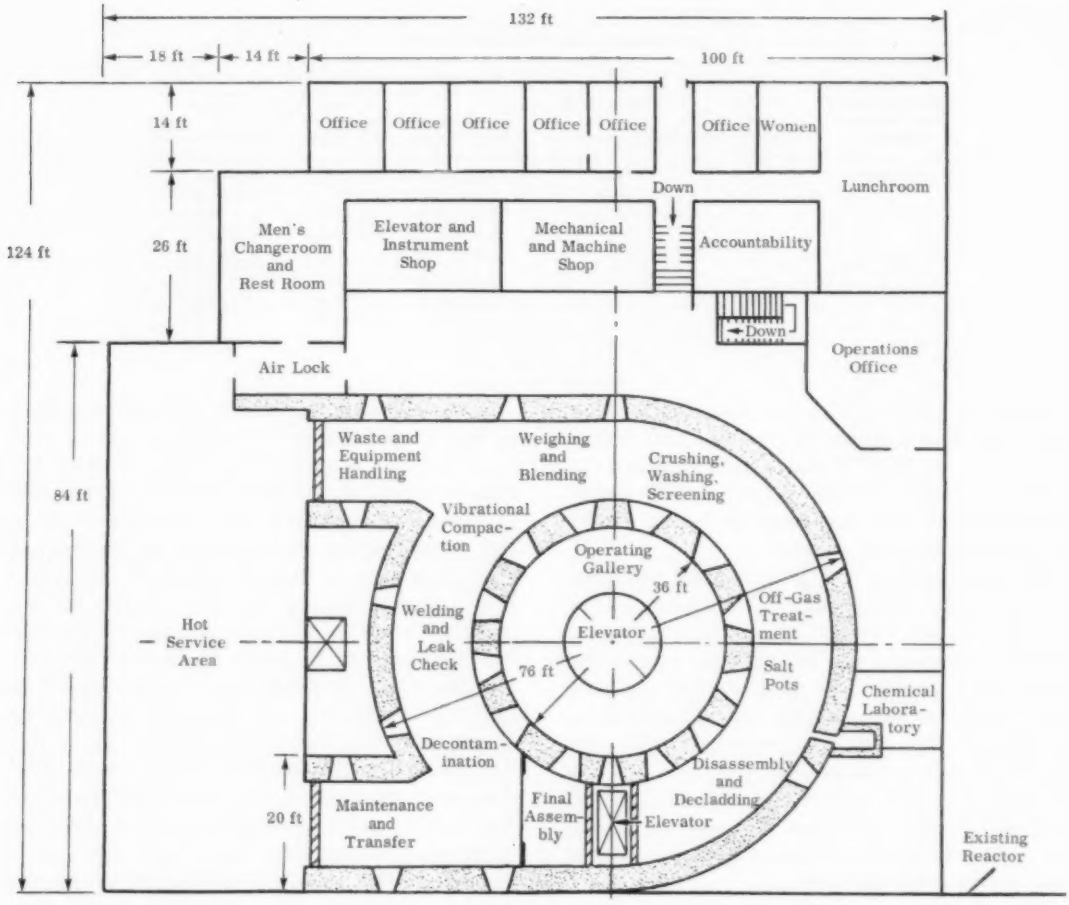

Fig. I-1 Close-coupled fuel-reprocessing-plant floor plan.[12]

Table I-11 FUEL-CYCLE SAVINGS WITH CLOSE-COUPLED PROCESSING WHEN ALLOWABLE INVESTMENT IS FIXED AT $6.2 MILLION[12]

Central-plant fuel exposure, Mwd/ton	Fission-product poison, DF	Savings, mills/kw(e)-hr		
		APWR reactor case	TWR reactor cases	
			S.S.-clad	Zirconium-clad
20,000	∞	0.066 to 0.223	0.010 to 0.155	−0.005 to 0.089
	6	0.037 to 0.186	−0.029 to 0.110	−0.064 to 0.045
Optimum	∞	−0.013 to 0.067	−0.007 to 0.088	−0.014 to 0.032
	6	−0.043 to 0.032	−0.050 to 0.044	−0.076 to −0.012

Economics of Irradiated Fuel Shipment

An analysis of the economics of irradiated fuel shipment has been made by Salmon.[13,14] Shipping costs have been recognized as an important economic component of the reactor fuel cycle, ranging from 1 to 10% of the total fuel-cycle costs. Most cost estimates have employed a nominal shipping cost of a certain number of dollars per kilogram of spent fuel, but this approach is not adequate for economic evaluation of alternative fuels with substantial dif-

ferences in element design and reactor exposure. In addition, the cooling time before shipping has an influence on shipping cost, so that costs associated with cooling and shipping should be considered together. The assumption of a nominal cooling time, say 120 days, has often been done, but this simple approach is also inadequate for evaluations of alternative fuel systems. Evaluation studies of shipping costs need to employ cost models capable of providing the computation of costs in terms of the several system variables over the full range of interest.

The present cost analysis and computational model was developed by relating system variables to their associated shipping costs, which were categorized as follows:

1. Handling cost, which covers rigging, loading, decontamination, and so forth.
2. Freight cost, which is the amount charged by the railroad or other carrier on the basis of distance and weight.
3. Cask cost, which covers the fixed charges on the capital invested in the casks.
4. Insurance cost, which covers insurance against loss of or damage to the fuel and cask during transit. Liability insurance is not included, on the basis that liability and indemnity provisions applying to the reactor will also cover the spent fuel during transit.

The associated cooling cost includes the inventory charge on the spent fuel for the cooling period and the capital and operating charges of the cooling facility required. If the fuel is leased from AEC, the current charge rate on the fuel inventory is 4.75%/year based on the value of the spent fuel. If the fuel is privately owned, the inventory charge rate will correspond to the fixed charge rate on working capital. (Details of the costs of cooling facilities are not included in this report.)

A conceptual cask design was adopted to suit the objectives of the study. This cask design was of conventional cylindrical configuration with components shown in Fig. I-2. Heat removal was by radiation from the fuel elements in the air-filled cask to the copper–boron divider plates and thence by conduction through the cask wall. At the outer surface of the cask, 6-in. fins dissipate the heat by natural convection to the environment. A construction cost of $1 per pound was assumed for the cask.

The features of the cask design conform to the requirements of the proposed AEC regulation (3), CFR Title 10, Part 72. The absence of mechanical cooling is in line with the provision of this AEC regulation which states that the full rate of heat removal must be maintained under accident conditions, in which all mechanical systems are assumed inoperative and all liquid coolant lost. A simplified mathematical model of the heat-transfer process was employed to relate allowable maximum temperatures to the heat-generation rate for the cask dimensions, from which the number of fuel elements per cask was derived. Shielding thickness was similarly related to the radiation source strength of the contained fuel elements and to allowable radiation outside the cask. The radiation source strength and heat-generation rate are dependent on the fuel burnup (irradiation exposure), specific reactor power, and cooling time. Fuel dimensions, weights, composition, and other characteristics are also pertinent to these determinations.

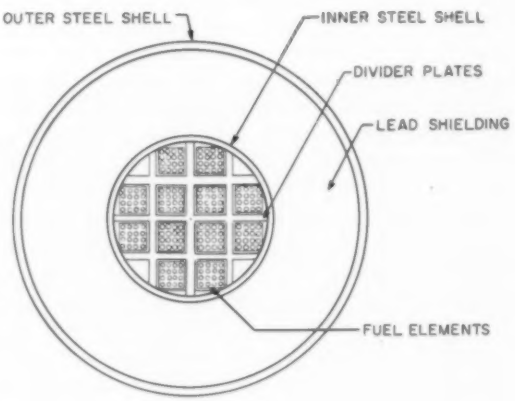

Fig. I-2 Reference design of spent-fuel shipping cask, showing typical arrangement of fuel elements. Each of the 10 fuel elements shown has 16 pins. Cooling fins on outer shell are not shown.

The analysis outlined above constitutes an identification of significant variables, assumption of physical and economic relations, and specification of the set of input data required for cost computations. The calculation sequence is shown in Fig. I-3. A computer code (MYRA) has been developed for the sequence shown, and it includes a subroutine (PHOEBE) for calculation of the radiation source strength and heat-generation rate. In the present analysis, fuel enrichment is not considered as a

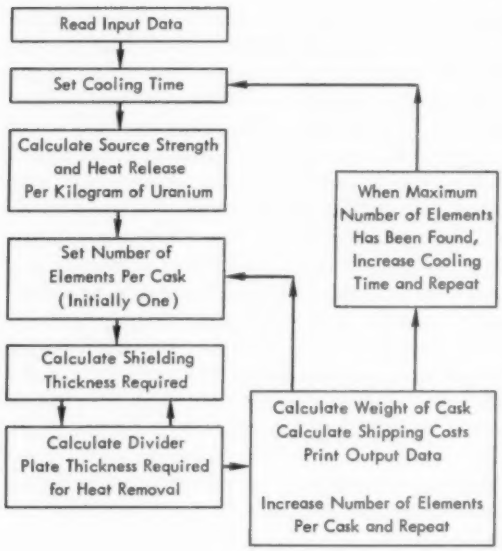
Read Input Data
Set Cooling Time
Calculate Source Strength and Heat Release Per Kilogram of Uranium
Set Number of Elements Per Cask (Initially One)
Calculate Shielding Thickness Required
Calculate Divider Plate Thickness Required for Heat Removal
When Maximum Number of Elements Has Been Found, Increase Cooling Time and Repeat
Calculate Weight of Cask
Calculate Shipping Costs
Print Output Data
Increase Number of Elements Per Cask and Repeat

Fig. I-3 Calculated sequence for fuel-shipping-cost code (MYRA).[13]

separate variable, but its influence is applied through the other variables specified. A criticality check was not incorporated in the code MYRA but was made separately.

Results obtained in the applications of this method of shipping-cost calculation illustrate significant features of the economics of spent-fuel shipment. In general, an optimum cooling time exists at which the sum of cooling and shipping costs are a minimum. In the case of a large desalination reactor, an optimum cooling time of about 160 days was found, with the curve rather flat for times ± 40 days around the optimum. The optimum cooling time is shorter for fuel of higher value or for higher inventory charge rates; it is longer for greater burnup or higher specific power.

An important effect on the cost of shipping itself is that due to variations in burnup and specific power. As an illustration, results are given in Fig. I-4 for a large desalination reactor at constant total thermal power and a constant 150 days' cooling. The combination of

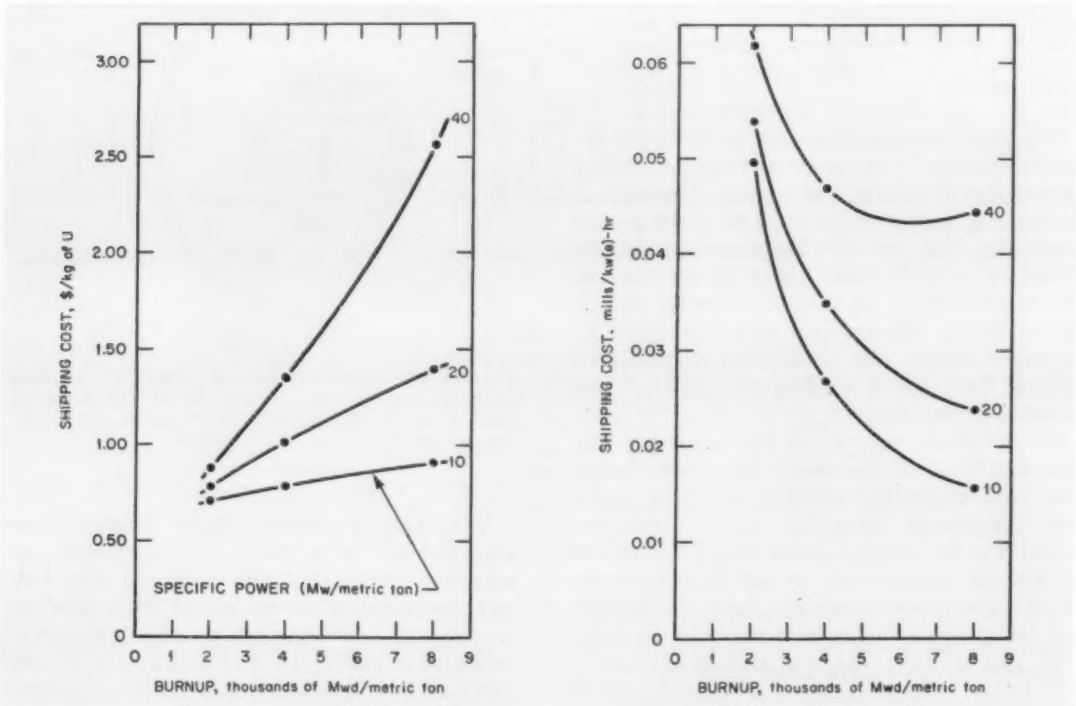

Fig. I-4 Effect of burnup on shipping cost for a reactor of fixed total power.[14] *As burnup increases, cost per kilogram increases, but cost per kilowatt-hour tends to decrease. Desalination reactor, 25,000 Mw(t). Cooling time, 150 days. Electrical efficiency, 0.30.*

high burnup and high specific power shows the largest costs of the range studied, with an optimum burnup shown for the highest value of the specific power parameter.

The optimum number of elements per cask was also examined and illustrated. The total shipping cost tends to decrease as the number of elements per cask is increased. The limiting number occurs when the limiting cask weight is reached, which for rail transport is about 120 tons. In the desalination reactor application, the curve of cost vs. the number of elements per cask showed a very flat minimum in the approach to the limiting value provided by the maximum allowable cask weight.

The ability to determine optima for system variables on an economic basis is the justification of such a detailed cost analysis. The analysis also affords a basis for appraising the economics of supplementary cooling means and the economic importance of the maximum allowable fuel temperatures.

For fuels with a combination of high burnup, high specific power, a large number of fuel pins per element, and a large mass of fuel per element, there is a minimum cooling time below which it is impossible to ship even one element per cask. (Presumably for fast reactors, where these fuel conditions are found and where the fuel value is also very high, the shipping and/or inventory costs will tend to be of greater importance than for most thermal-reactor fuel.)

Other considerations involved in the complete analysis of shipping costs but not optimized in the code MYRA are (1) a check for noncriticality, (2) the use factor of casks and determination of their optimal number, and (3) the overall fuel-management scheme, which includes scheduling at the reprocessing plants, turnaround charges, etc. In continuing work, more comprehensive analyses are planned.[13,14]

Symposia on Reactor Fuel Shipment

An international symposium was held at Albuquerque, N. Mex., under the joint sponsorship of AEC and the Sandia Corporation, January 12–15, 1965. All papers given at the symposium are published in the *Proceedings of the International Symposium for Packaging and Transportation of Radioactive Materials*.[15] The papers cover topics in design and testing of casks and in shipping procedures and regulations. Safety analysis was the chief focus of these papers, and the reader is referred to the review of the symposium in the Summer 1965 issue of *Nuclear Safety*.[16]

The Summer 1965 issue of *Reactor Fuel Processing*[17] cited the publication of eight papers on the subject of shipping of radioactive material originally presented at the Fifty-Seventh Annual Meeting of the American Institute of Chemical Engineering at Boston in December 1964. One of these papers dealing with an economic evaluation was that of Salmon[13] reviewed above.

Patents Concerning Processing

A Patented Process Combining Aqueous and Volatility Methods

A German patent has been issued to the General Electric Company on a processing method that combines aqueous solvent extraction and fluoride-volatility steps.[18] The merit of this process is said to be that it eliminates several of the steps of the conventional aqueous method, with notable reduction in waste-storage volumes. The process appears to incorporate some of the best-demonstrated steps of volatility processing. A fluid-bed fluorination and a fractional distillation were commercially employed in General Chemical's Metropolis plant for producing purified uranium hexafluoride from ore concentrates.[19] Pilot-plant studies of fission-product decontamination of UF_6 have been performed at AEC national laboratories (ANL, BNL, ORNL).[20,21]

In the patented process,[18] acid dissolution is carried out on the fuel, and a single solvent-extraction cycle (three columns) is used to yield three separated aqueous streams containing, respectively, the bulk of the fission products, plutonium nitrate, and uranyl nitrate. In this single solvent-extraction cycle, fission-product decontamination is not complete: ruthenium, niobium, and/or zirconium accompany the uranium. The two streams containing, respectively, the bulk of the fission products and the plutonium are treated subsequently by conventional aqueous methods. The uranium stream is treated by fluid-bed volatility methods to yield highly decontaminated uranium hexafluoride product. These steps include fluid-bed

Table I-12 AEC-OWNED PATENTS PERTINENT TO REACTOR FUEL PROCESSING[22,23]

Patent No.	Issuance date	Patent title
3,164,440	Jan. 5, 1965	Gas-Solids Contacting Method
3,164,462	Jan. 5, 1965	Preparation of Thorium Metal from the Oxide
3,165,376	Jan. 12, 1965	Process for Separation and Recovery of Volatile Fluoride Impurities from Uranium Hexafluoride Containing the Same
3,165,377	Jan. 12, 1965	Separation of Stainless Steel from a Nuclear Fuel
3,165,417	Jan. 12, 1965	High Strength Beryllia Articles
3,165,422	Jan. 12, 1965	Ceramic Coated Fuel Particles
3,167,695	Jan. 26, 1965	Liquid Level Capacitance Probe
3,169,057	Feb. 9, 1965	Separation of Plutonium Uranium and Fission Products from Each Other
3,169,117	Feb. 9, 1965	Nuclear Reactor Fuel Paste Composition
3,170,759	Feb. 23, 1965	Method of Making Plutonium Monocarbide
3,170,788	Feb. 23, 1965	Uranium Base Alloy
3,170,812	Feb. 23, 1965	Method of Vitrifying Ceramic Coatings
3,170,843	Feb. 23, 1965	Paste Reactor
3,171,417	Mar. 2, 1965	Method of Making Plutonium Oxide Spheres
3,171,715	Mar. 2, 1965	Method for Preparation of Spherical Thorium Dicarbide and Thorium-Uranium Dicarbide Particles
3,171,815	Mar. 2, 1965	Method for Preparation of Thorium Dicarbide and Thorium-Uranium Dicarbide Particles
3,173,973	Mar. 16, 1965	Graphite Dispersion
3,173,757	Mar. 16, 1965	Purification of Strontium Solutions by Ion Exchange
3,174,818	Mar. 23, 1965	Reducing Corrosion of Stainless Steel in Hot Nitric Acid Solutions by Adding Carbon Black or Elemental Sulfur to the Solution
3,174,834	Mar. 23, 1965	Fluidized Bed Reactor
3,175,922	Mar. 30, 1965	Method for Coating Actinide Particles
3,177,553	Apr. 13, 1965	Apparatus for Solvent-Isostatic Pressing
3,178,256	Apr. 13, 1965	Method for Separating Transplutonium Elements from Rare Earth Fission Products
3,178,258	Apr. 13, 1965	Separation of Plutonium Hexafluoride from Uranium Hexafluoride by Selective Sorption
3,178,259	Apr. 13, 1965	Nitrided Electrode Process of Preparing Uranium Mononitride
3,179,501	Apr. 20, 1965	Countercurrent Nuclear-Fuel Liquid-Liquid Extraction Apparatus
3,179,503	Apr. 20, 1965	Extraction of Cesium from Aqueous Solution Using Phenols
3,179,722	Apr. 20, 1965	Method of Preparing Spherical Nuclear Fuel Particles
3,179,723	Apr. 20, 1965	Method of Forming Metal Carbide Spheroids with Carbon Coat
3,180,704	Apr. 27, 1965	Process of Making Actinide Sulfide and Similar Compounds
3,180,756	Apr. 27, 1965	Copper Metallizing of Alumina Ceramics

drying and calcination of the uranyl nitrate solution; fluid-bed conversion of the dry uranium compounds to hexafluoride; and removal of the less volatile fluorides of ruthenium, niobium, and zirconium from the uranium hexafluoride by partial condensation and/or fractional distillation.[18]

AEC-Owned Patents Made Available for Licensing

The AEC has announced patents newly available for licensing.[22,23] The titles considered relevant to fuel processing are listed in Table I-12.

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Section

II

Reactor Fuel Processing

Research and Development on Aqueous Processing

Methods for the dissolution of sintered aluminum powder and of high-strength aluminum fuel alloys have been studied; solvent-extraction process improvements have been studied and applied. Work is reported on the recovery of curium for space power applications and research.

Preparation for Fuel Processing

By C. E. Stevenson

Sintered-aluminum-powder fuel cladding may be dissolved in mercury-catalyzed H_2SO_4. Certain aluminum alloys are more resistant to attack by mercury-catalyzed HNO_3 than is pure aluminum.

Dissolution of Aluminum Fuel Compositions

It was previously noted that sintered aluminum powder (SAP), an aluminum fuel structural material exhibiting adequate strength for use in fabricating fuels for organic-cooled reactors, dissolved much more slowly in mercury-catalyzed HNO_3 than did high-purity aluminum or its alloys, which are conventionally used for making fuels for water-cooled reactors such as the Materials Testing Reactor (MTR).[1] Further work on dissolving SAP has been carried out by Beone[2] using mercury-catalyzed H_2SO_4 as the dissolution reagent. Dissolution of SAP cladding in $3N$ to $6N$ H_2SO_4, catalyzed by Hg^{2+}, is much faster than in HNO_3, and attack on the fuel contained in the cladding is minimal. The Al_2O_3 portion of the cladding is not soluble even in boiling solution. The reaction is complicated because of the loss of $HgSO_4$ by precipitation, decrease in the rate of dissolution as Al_2O_3 content is increased, and decreasing solubility of $Al_2(SO_4)_3$ as H_2SO_4 concentration is increased. About 450% excess of the stoichiometric amount of H_2SO_4 appears to be desirable.

At the Idaho Chemical Processing Plant, work previously noted[3] on the effects of minor constituents on the dissolution of aluminum alloys in HNO_3 has been resumed. Bower[4] reports that fuel plates proposed for use in the Advanced Test Reactor (ATR) and composed of a core of 35 wt.% U_3O_8 in aluminum alloy X8001 clad with either aluminum alloy 6061-0 or X8001 dissolved at rates of 14 mg/(cm^2)(min) in $6.6M$ HNO_3 containing $0.05M$ $Hg(NO_3)_2$ at 90°C up to the time that one-half of the plate was dissolved. The rate was somewhat lower thereafter but was believed to be more than adequate for conventional processing. Boron carbide (initially present as a <325-mesh B_4C powder) at a concentration of 0.19% in the core left no detectable residue. A similar fuel plate containing a UAl_3–X8001 core dissolved at a somewhat lower but still adequate rate. More recently Buckham[5] has reported that type 5356 aluminum containing 5% magnesium, a material of interest for side-plate construction, dissolves similarly to type 6061 aluminum alloy.

Treatment of Carbide and Graphite Fuels

Uranium-impregnated graphite fuels and those containing the carbides of uranium, plutonium, or thorium are difficult to process by aqueous techniques because of the refractory nature of these materials, their resistance to attack by acids and alkalis, and the insoluble residues that may accompany fissionable-material solutions obtained by treating such fuels. Among

the techniques proposed to put the fissionable materials present in a form suitable for solvent extraction are (1) grinding and acid leaching, (2) combustion and leaching, and (3) chemical disintegration, including hydrolysis.[6] A modified combustion technique has been proposed by Lopez-Menchero and Rometsch.[7] The graphite compacts, amorphous and pyrolytic carbon, and SiC layers in which the fissile and fertile elements or their carbides are included are oxidized under molten salts with oxygen, or with the oxygen released in the thermal decomposition of NO_2. The residue remaining is leached by mineral acids (HNO_3) to produce a solution suitable for solvent extraction.

Solvent-Extraction Processes

By C. E. Stevenson

A flow sheet is given below for the reduction of plutonium by U(IV) which is applicable to an existing pulsed-column Purex plant (Hanford), and it is noted that plutonium may also be reduced by hydrogen. It is shown that sparging of extraction-process solutions by NO should improve ruthenium decontamination by a small factor. Solvent properties and distribution data are given for plutonium recovery by an Alamine 336–dibutyl carbitol system.

Tetravalent Uranium for Reduction of Plutonium in TBP Processing

In the Purex process for uranium and plutonium recovery and decontamination by Bu_3PO_4 (TBP) extraction, the separation of plutonium from uranium is normally effected by treatment of the solvent phase with Fe^{2+}, which reduces plutonium and permits it to be selectively stripped from a solvent phase containing both uranium and plutonium. This, however, introduces iron salts into the aqueous wastes. An alternative procedure involves reduction with tetravalent uranium, which introduces no foreign ions. Process modifications that would be required to adopt this procedure to Purex processing at the Savannah River Plant, in which mixer–settler contactors are used, were described in the Summer 1964 issue of *Reactor Fuel Processing*.[8] Mendel, at Hanford, has more recently described a flow sheet appropriate to the use of tetravalent uranium in the Hanford pulsed-column Purex plant.[9] In this flow sheet, contrary to that proposed for Savannah River, an aqueous stream containing U(IV) and hydrazine is contacted with Purex solvent and both phases are introduced to the partition column at the uranium- and plutonium-bearing solvent feed point. Although introduction above the feed point might be preferable and is done in the mixer–settlers at Savannah River, no such point is available in the Hanford column. Addition of U(IV) in aqueous form only was not considered because the reduced uranium would presumably follow the aqueous phase into the scrub portion of the column. The mixed stream provides a sufficiently direct contact with the solvent phase in the column to ensure plutonium reduction. The partition-column portion of the proposed flow sheet is shown in Fig. II-1.

The tetravalent uranium solution, containing N_2H_4 to reduce NO_2^- that might be present in the solvent, is blended in a tank with 31 times its volume of Purex solvent (30% TBP in hydrocarbon diluent) under conditions that allow about a 1-hr holdup to permit its extraction. Laboratory tests[9] showed that about 30% of the U(IV) was immediately oxidized but that gen-

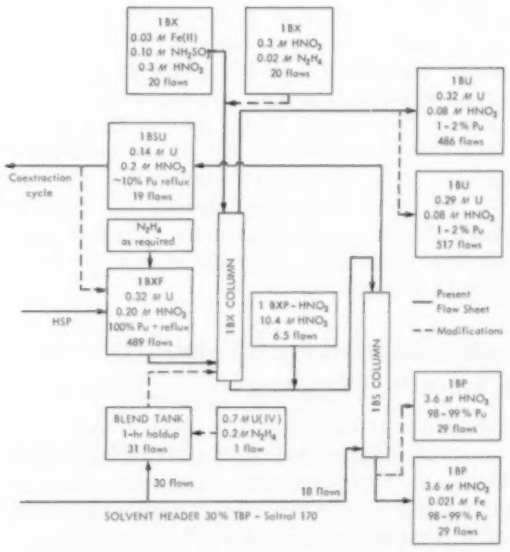

Fig. II-1 Purex partition-cycle flow sheet using tetravalent uranium.

erally a major proportion was available for plutonium reduction after holding from 5 to 7 hr. The presence of NO_2^- is also minimized by introducing a $N_2H_4-HNO_3$ stream to the top of the plutonium separation column. Laboratory tests indicated that U(IV) was sufficiently stable in this column to ensure its presence throughout the 15-min residence time of the organic phase.

In other laboratory tests[9] the effectiveness of U(IV) was compared to that of Fe(II) for plutonium reduction under conditions assumed to exist at the bottom of the column. Equal volumes of synthetic IBY-column feed solution [0.21*M* HNO_3 and 0.32*M* $UO_2(NO_3)_2$ containing Pu(IV) in 30% TBP-diluent mixture] were contacted with agitation, and plutonium distribution ratios were determined after 2- and 10-min contact times at 45°C. With Fe^{2+}, distribution ratios were of the order of 0.01 to 0.09, compared to 0.008 to 0.02 observed for U(IV), which indicated that the uranium salt was at least as effective.

In connection with the reduction of plutonium to permit its separation from uranium, a recent article by Rainey[10] of Oak Ridge National Laboratory is of interest. His tests have shown that Pu(IV) may be catalytically reduced by hydrogen gas. A gas mixture containing 4% hydrogen in argon was passed concurrently with equal volumes of a solvent solution (30% TBP in diluent) containing 95 g of uranium per liter, 1 g of Pu(IV) per liter, and 0.1*M* HNO_3 and an aqueous solution of 0.5*N* HNO_3 through a column packed with Al_2O_3 pellets impregnated with 5% platinum. The liquid holdup time in the column was about 10 min. Over 99% of the plutonium and less than 1% of the uranium were reduced. The test was performed simply to indicate feasibility. In a plant process it is assumed that use of a holding reductant such as N_2H_4 might be necessary.

Ruthenium Decontamination in Extraction Processes

Workers at Harwell have, over a period of years, reported extensively on causes for poor ruthenium decontamination and on means of minimizing poor ruthenium decontamination in solvent-extraction processes.[11] Lyon and Scargill have recently published a contribution on the treatment of ruthenium-bearing uranium solutions with nitrous acid in order to reduce the extractability of ruthenium.[12] Their studies were on the formation of nitrous acid by sparging HNO_3 solutions with NO and on the distribution of ruthenium by paper chromatography.

The conversion of nitrosylruthenium nitrato complexes to the more stable RuNO nitro complexes by HNO_2 treatment should improve ruthenium decontamination of uranium since the dinitro complexes have lower distribution coefficients than some of the nitrato complexes in contact with TBP and Butex solvents.

A suitable treatment to effect the formation of greater than 90% RuNO nitro complexes in 3*M* $HNO_3-1.25M$ $UO_2(NO_3)_2$ solutions was found to consist of treating the RuNO nitrato complexes with a concentration of HNO_2 greater than 0.15*M* HNO_2 at 50 to 60°C for about 3 hr. Under these conditions, although a large proportion of the TBP-extractable dinitro complex is formed, its distribution coefficient vs. 30% TBP diluent is less by a factor of about 6 than that of the nitrato complexes assumed to control the decontamination factor. Because of the probable presence of 60 to 80% of the ruthenium as RuNO nitro complexes formed in the dissolution process, this nitrous acid treatment would only result in a twofold to fourfold improvement of the decontamination factor for ruthenium.

Extraction with Amine–Ether Systems

The use of tertiary amines as solvents for the extraction processing of fissionable materials is of increasing interest. Italian workers have been particularly active in this field as discussed in previous issues of *Reactor Fuel Processing*.[13] Recent work from Harwell by Lane, Pilbeam, and Fletcher[14] and Jenkins et al.[15] has described some stages in the development of an amine extraction process suitable for recovery of plutonium from a hypothetical fast reactor fuel composed of 25% plutonium–75% uranium. In the primary cycle of the process envisaged, as shown in Fig. II-2, only the plutonium is extracted, and the uranium passes into the aqueous raffinate with the fission products.

One disadvantage of amine systems is their tendency for third-phase formation, and the consequent low loading achievable for fissionable materials. Although long-chain alcohols alleviate third-phase formation, they may not be adequately radiation-stable. Lane, Pilbeam,

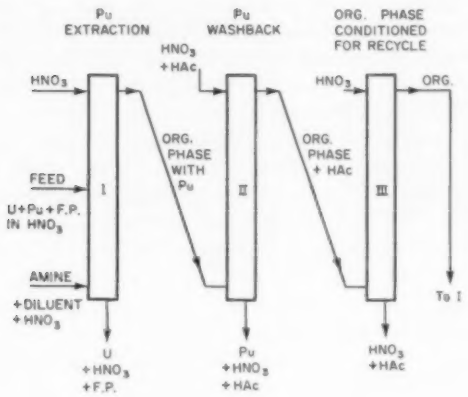

Fig. II-2 Outline flow diagram for separation of plutonium by an amine system.[14] (Courtesy of Atomic Energy Research Establishment, Harwell.)

and Fletcher[14] propose the use of the ether dibutyl cellosolve (DBC) to dilute an amine solvent such as Alamine 336. In their tests such a system showed reasonable thermal and radiation stability, although a 10% solution of Alamine 336 was completely destroyed by $3M$ HNO_3 after 120 hr at 100°C. Long-chain carboxylic acids were formed. Under irradiation (100 Mrads), primary and secondary amines, in amounts equal to about 5 to 10% of the tertiary amine present, were formed, but there was no abnormal retention of U(VI) or Pu(IV) by the degradation products. Compared with aliphatic hydrocarbon diluents, DBC reduces the tendency to third-phase formation and eliminates it entirely at HNO_3 concentrations of greater than $2N$. However, DBC is inferior in this respect to more aromatic diluents.

The second report[15] on this subject (by Jenkins et al.) comprises distribution coefficients for uranium, plutonium, and HNO_3 with 5 to 15% Alamine 336 solutions in DBC and considers methods of reextraction of plutonium from the solvent phase. The distribution coefficients, some of which are shown in Fig. II-3, as functions of concentrations of amine in the diluent, indicate that a flow sheet of the type desired for plutonium recovery will be feasible. The use of either ferrous sulfamate or acetic acid to backwash plutonium from the organic phase was considered. A marked time dependence of the distribution coefficient was observed for the use of ferrous sulfamate, which implied that the use of long-residence-time contactors might be necessary. Attention was therefore directed toward the use of CH_3COOH as a complexing agent. With $0.5M$ to $3.0M$ CH_3COOH alone, on successive backwashing either a white precipitate or a second organic phase is formed. Mixtures of CH_3COOH and HNO_3 can be used, however, if just enough HNO_3 is added to prevent the formation of two organic phases (higher concentrations tend to reduce extractability from the amine). For example, stripping reagents composed of $0.05M$ to $0.1M$ HNO_3 and $0.5M$ to $1.0M$ CH_3COOH appear to be satisfactory.

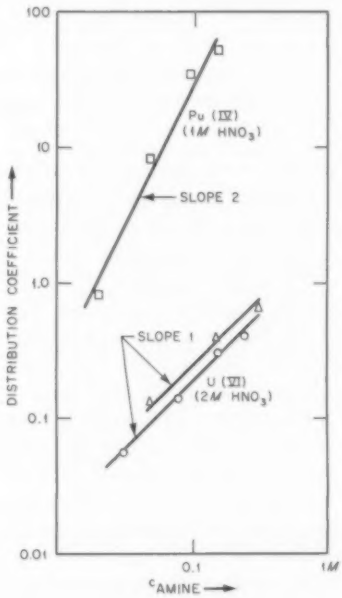

Fig. II-3 The variation of the log of the distribution ratios for uranium and Pu(IV) with the log of the tertiary amine concentration.[15] (Courtesy of Atomic Energy Research Establishment, Harwell.)

Separation of Americium and Curium from Irradiated Plutonium

By C. E. Stevenson

The isotope ^{244}Cm is of interest for use as a source of power for space vehicles because of its relatively long (18-year) half-life, high

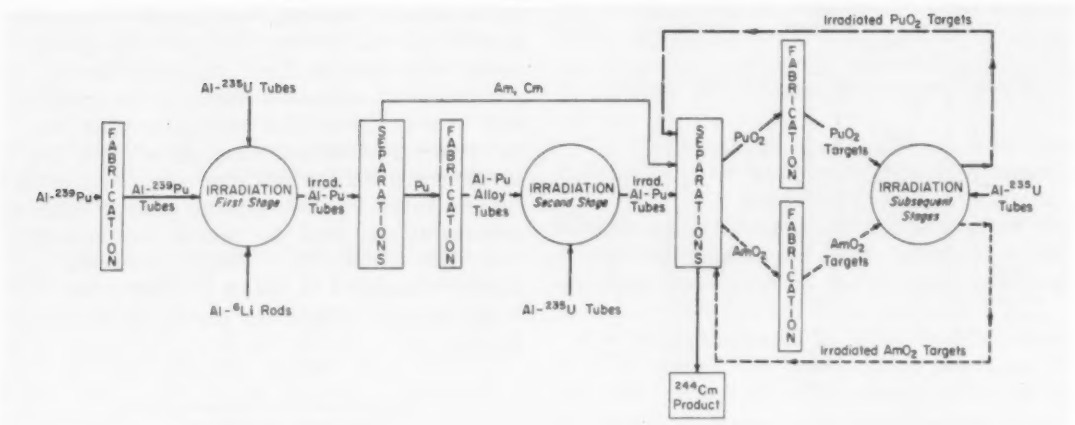

Fig. II-4 Process for producing ^{244}Cm in several irradiation stages.[17] (Reprinted from Nuclear Applications, *Vol. 1, No. 4.)*

specific power, and potential availability in significant amounts from the prolonged irradiation of plutonium. It is one of the transplutonic elements that is now becoming available from the U. S. transuranic-element production program, involving Hanford, Savannah River, and the Oak Ridge National Laboratory, which was described in the Spring 1964 issue of *Reactor Fuel Processing.*[16] Groh et al.[17] have recently published a description of Savannah River plans and achievements in the pilot production of 3 kg of ^{244}Cm as part of the overall program. This material will be available for development and demonstration of SNAP systems, and fractional gram quantities of americium and curium have already been carried through the processing steps.

The overall process, shown in Fig. II-4, involves a first-stage irradiation of plutonium (principally ^{239}Pu), separation of initial amounts of americium and curium, a second-stage irradiation of plutonium (now containing much ^{242}Pu), and further separations followed by later stages of irradiation of ^{242}Pu and ^{243}Am targets and their processing. Plutonium is recovered and purified in two cycles of TBP solvent extraction and is then converted to metal through ion exchange, precipitation, and reduction processes.

Americium, curium, and some rare-earth fission products are reclaimed from the plutonium-process wastes by batch extraction into 50% TBP in *n*-dodecane. The stripped product is concentrated and then purified by three cycles of solvent extraction with tertiary amine

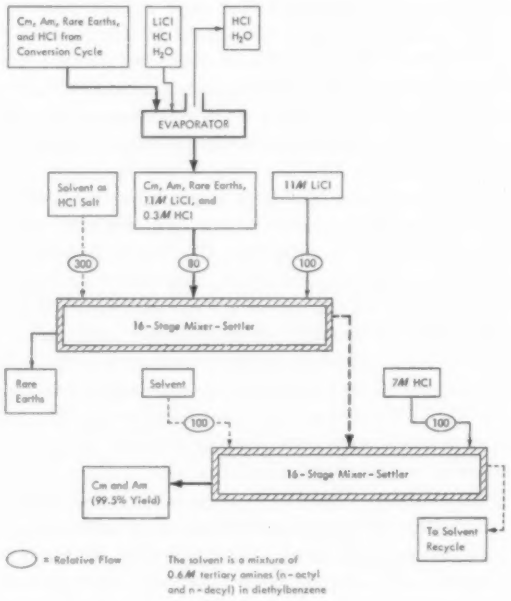

Fig. II-5 Purification of americium and curium by solvent extraction with tertiary amines.[17] (Reprinted from Nuclear Applications, *Vol. 1, No. 4.)*

(*n*-octyl and *n*-decyl) chlorides in diethylbenzene. The first cycle converts the nitrate salts to chlorides. The flow diagram for the subsequent purification cycle is shown in Fig. II-5.

A miniature mixer–settler pilot plant was constructed for demonstration of the amine process. This has performed quite satisfac-

torily, and greater than gram quantities of ^{244}Cm have been purified. In addition to testing the process, the equipment served also to test the alpha containment provisions, fabrication techniques, and construction materials. Tantalum was the only material that withstood corrosion during these demonstration tests. In operations involving gram quantities of ^{244}Cm, losses of curium have been only 0.46%, and factors for decontamination from zirconium, ruthenium, cerium, and europium have been $>10^6$, $>4 \times 10^6$, 1.5×10^8, and $>8 \times 10^5$; all of which are in excess of process requirements.

The separation of americium from curium in the solvent-extraction product is effected by precipitation of the americium double carbonate $[K_5AmO_2(CO_3)_3]$. The HCl solution of americium and curium after concentration is added to saturated K_2CO_3 solution to produce concentrations of about 10 g each of americium and curium per liter. Then KOCl or $K_2S_2O_8$ is added to oxidize americium to the pentavalent state, and the americium double carbonate is filtered off after 2-hr digestion at 85°C. In tests of this step, the separated curium contained less than 0.5% of the americium.

In supporting work on the solvent-extraction purification phase of this process, Roth and Henry[18] have reported equilibrium distribution coefficients for americium, curium, europium, and HCl in systems composed of $9M$ to $11M$ LiCl, $0M$ to $0.35M$ HCl, and small amounts of $SnCl_2$ vs. 30 vol.% of the tertiary amine Alamine 336 (or Adagen 364) in diethylbenzene. Equations for the distribution data obtained are as follows:

For HCl,

$$E_a^\circ = \exp(-7.4y_1 + 0.85L - 6.23)$$

For americium,

$$E_a^\circ = \exp(-11.4y_1 + 1.97L - 18.73)$$

For europium,

$$E_a^\circ = \exp(-11.5y_1 + 1.865L - 22.115)$$

For curium,

$$E_a^\circ = \exp(-10.35y_1 + 1.675L - 15.965 - 6S \cdot L + 52S)$$

where y_1 is the equilibrium molar concentration of HCl in the organic phase, L is the aqueous LiCl molar concentration, and S is the organic Sn^{2+} or Sn^{4+} molar concentration.

The presence of either stannous chloride, added to scavenge radiolytically produced chlorine and HOCl, or stannic chloride was found to affect the distribution of curium, but not that of HCl. This behavior may be tentatively interpreted as implying complex formation (between curium and tin) similar to that observed between uranium and tin.[19] No data were obtained for the effect of tin on americium or europium distribution.

Ion-exchange processes are also much used to effect the separation and purification of americium and curium, particularly on a laboratory scale. Bochkarev and Voevodin[20] have recently reported on the use of CH_3OH containing HNO_3 for the chromatographic elution of americium and curium from the anion resin AV-17 or Dowex 1-X8. When resin AV-17 was used, it was established that increasing the concentration of HNO_3 from $0.1M$ to $1.6M$ and the concentration of CH_3OH from 80 to 95% in the mixture led to significantly increasing the coefficient of separation of americium and curium. These separation coefficients appeared to be two to three times greater than values obtained by other workers utilizing elution by nitrate, lactate, or ammonium α-hydroxyisobutyrate. A $0.1M$ HNO_3 concentration was recommended to minimize the separation time when the methanol eluant was used.

Plant and Equipment Design and Operation

By D. M. Paige

The pilot-plant electrolytic dissolver system developed at the Idaho Chemical Processing Plant and described in the Fall 1963 issue of *Reactor Fuel Processing*[21] has now been operating for some time on a variety of simulated stainless-steel fuels. Investigators[4] report on several of these runs that have been fairly successful. Table II-1 shows the conditions of some typical runs. They report current utilization rates of stainless steel to be 0.71 g/amp-hr for HTRE fuel, 1.22 g/amp-hr for PM-3A elements, and 0.53 g/amp-hr for APPR elements. These rates correspond to 21 to 46 kg of uranium per day for a full-scale plant dissolver.

Table II-1 SUMMARY OF CONDITIONS FOR RUNS 8 TO 10 IN THE MODEL 2 ELECTROLYTIC DISSOLVER[4]

Conditions	Run 8	Run 8C	Run 9	Run 10A	Run 10B	Run 10C	Run 10D	Run 10E	Run 10F
Duration, hours	41.2	18.4	42.0	34.8	3.5	2.5	1.7	5.8	12.7
Dissolver potential, volts	19.2	19.4	19.0	19.1	19.0	24.0	23.0	19.0	19.0
Recirculation rate, liters/min	5.9	5.9	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Dissolvent composition:									
Stainless steel, g/liter	54.3	54.3	52.2	51.9	28.1	27.2	29.6	38.2	47.7
HNO_3, *M*	4.7	4.5	4.5	4.7	6.3	6.4	6.1	5.6	5.0
Dissolvent temperature:									
Dissolver inlet, °C	28	35	40	40	37	27	27	32	33
Dissolver outlet, °C	52	54	61	62	64	64	71	63	63
Dissolver pressure, psia	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0
Acid feed concentration, molar HNO_3	8.4	8.4	8.1	8.2	8.2	8.2	8.2	8.2	8.2
Acid feed rate, liters/min	5.7	2.8	9.0	4.5	10.7	13.0	17.5	7.4	6.3
Type of fuel element dissolved	HTRE	HTRE	PM-3A	APPR*	APPR*	APPR*	APPR*	APPR*	APPR*

*Welded APPR plate bundles.

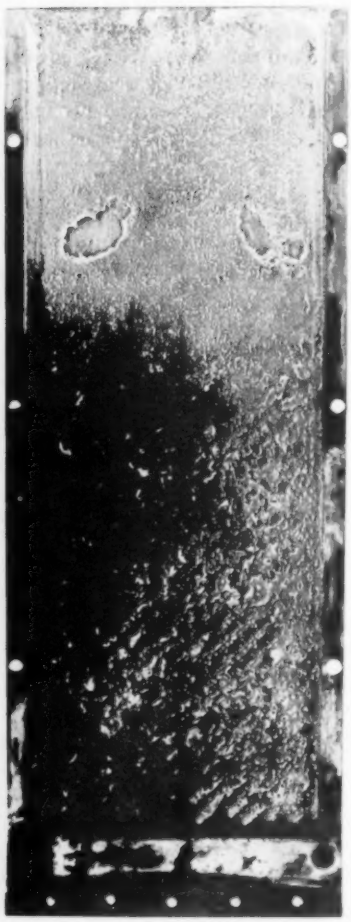

Fig. II-6 Gelatinous deposit on cathode of pilot-plant electrolytic dissolver.[4]

In these runs a problem of coating formation on some of the metal dissolver surfaces was noted. A loss of cooling capacity in the product cooler was traced to the formation of this residue on the heat-transfer surface. The dissolver cathode was also found to be coated with a yellow-colored gelatinous deposit (see Fig. II-6). The coating could be removed by cold 40% hydrofluoric acid, but not by cold or hot nitric acid, sulfuric acid, or combinations of the two. Preliminary indications are that this deposit is a siliceous compound formed from the 0.5% silicon in the stainless steels.

Some further corrosion results indicate that the platinum anode is corroding at a rate of 0.1 mil/month, and the niobium cathode, at a rate of 0.2 mil/month.

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

By J. J. Barghusen

Volatility Processes for High-Enriched Fuels

A fluid-bed volatility process for the recovery of uranium from highly enriched uranium-alloy fuels is being developed at Argonne National Laboratory (ANL).[1] Current studies are being made with uranium–aluminum and uranium–zirconium alloys. The process employs three principal steps in which chemical separation of the fuel constituents is achieved by selective volatilization of chlorides and fluorides. In the first step, separation of the alloying and cladding material (aluminum or zirconium) from uranium is achieved by reacting the fuel material with hydrogen chloride gas at 350°C while the fuel is immersed in a fluidized bed of refractory alumina particles. Separation of the alloying and cladding elements occurs by formation of volatile $AlCl_3$ and $ZrCl_4$, which are converted to the oxides in a separate pyrohydrolysis reactor. Uranium is converted to solid UCl_3 during hydrochlorination and, for the most part, remains associated with the fluid-bed material. Any uranium chloride entrained in the gas stream leaving the fluid-bed reactor is retained on a high-temperature packed-bed filter in series with the fluid-bed reactor.

In the second step the UCl_3 in the fluid-bed reactor and packed-bed filter is converted to UF_4 by reaction with hydrogen fluoride gas. Recovery of uranium as UF_6 is achieved in the third step by the reaction between UF_4 and fluorine at 250 to 500°C.

The results of preliminary studies in a 1½-in.-diameter fluid-bed reactor were published recently.[2] These studies were concerned with defining the behavior of uranium in the process system and with establishing conditions that would result in a minimal amount of unrecoverable uranium. Most of the results from these studies have been previously reviewed in *Reactor Fuel Processing*.[3–5]

Pilot-Plant Demonstration Tests

A pilot-plant facility has been constructed at ANL[1] to demonstrate the processing of up to 30 kg of uranium–zirconium alloy and up to 14-kg charges of uranium–aluminum alloy. A description of the pilot-plant facility and details of experimental results from reprocessing tests with simulated alloy fuel materials have been reported by Holmes, Stethers, and Barghusen.[6] The progress of engineering development work on the pilot-plant facility has been reviewed in the Summer 1965 and Fall 1964 issues of *Reactor Fuel Processing*.[3,4]

Of prime importance in the pilot-plant program was the demonstration of uranium recoveries of greater than 99% of the uranium charged to the system. Uranium losses were primarily due to (1) passage of uranium through the packed-bed filter during the hydrochlorination step and (2) retention of uranium by the alumina in the fluid bed and filter bed after the fluorination step. Results of pilot-plant tests have shown that 99% of the uranium in the alloy fuel material can be recovered as UF_6 (see Table III-1) by employing a two-temperature fluorination procedure. The fluorination procedure involved introducing dilute fluorine (6 vol.% fluorine in nitrogen) into the fluid-bed reactor at 250°C and then slowly raising the temperature of the bed to 500°C over a 2- to 6-hr period. Fluorination was completed by operating with 30 to 60 vol.% fluorine under static-bed conditions for an

Table III-1 URANIUM BALANCE FOR A PILOT-PLANT RUN[6]

	Weight, g	Total weight, g	Uranium charge present, %
Total uranium charge		841.3	100
Uranium recoverable		836.0	99.3
In UF_6 trapping system	832.9		
In bed samples	3.13		
Uranium lost		4.7	0.6
To pyrohydrolyzer	3.17		
To reactor bed	0.62		
To filter bed	0.9		
To scrub system	0.001		
Uranium accounted for		840.7	99.9

additional 2 hr at 500°C. In general, the final uranium content of the reactor and filter-bed materials was less than 0.2% of the total quantity of uranium charged to the reactor.

In early runs[1,6] with aluminum–uranium alloy fuels, the uranium loss to the pyrohydrolysis reactor by transport through the packed-bed filter was relatively high (>2%). In these tests a filter-bed depth of 4 to 8 in. of 14- to 28-mesh alumina was used. In subsequent tests wherein 11- to 12-in.-deep beds of 14- to 48-mesh alumina particles were used, the uranium loss to the pyrohydrolysis reactor was reduced to less than 0.6% of the uranium charged to the facility. It is expected that uranium loss[6] by this mode could be further reduced by increasing the depth of the packed bed to greater than 12 in. In tests with zirconium-alloy fuel, it was observed that the uranium loss by transport through the packed-bed filter to the pyrohydrolysis reactor was uniformly low (<0.6%) and was essentially independent of the depth of the filter bed.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

SOLVENT EXTRACTION–VOLATILITY PROCESS PATENT

A German patent[7] on a process for the recovery and purification of uranium from aqueous solutions based on the use of calcination and fluorination techniques has been assigned to the General Electric Company. The process utilizes an aqueous head-end step wherein uranium and plutonium from UO_2 fuel are separated from the bulk of the fission products by solvent extraction. Plutonium is recovered from the organic solvent by countercurrent extraction with a dilute nitric acid solution containing ferrous ions. Final plutonium purification and recovery are effected by anion exchange from a plutonium nitrate solution containing 7.5*M* nitric acid. Uranium and selected fission products (principally ruthenium, zirconium, and niobium) are stripped from the organic phase by countercurrent extraction with a dilute (0.01*M*) nitric acid solution. This solution is then evaporated to a concentrated solution of approximately 60% uranyl nitrate hexahydrate. Conversion of the uranium and selected fission products to oxides is effected by evaporation of the solution and calcination of the solids at 300°C. A certain amount of fission-product ruthenium is volatilized during the calcination. The calcined solids are fluorinated directly in a single reaction step, using elemental fluorine at temperatures between 300 and 600°C. An alternative fluorination scheme involves the use of hydrogen fluoride at 250 to 350°C prior to fluorination with fluorine. The products from the fluorination step consist primarily of a gaseous mixture of uranium hexafluoride and the fluorides of the selected fission products. Initial separation of the UF_6 from the volatile fission-product fluorides is achieved by partial condensation of the less volatile fluoride species. Final purification of UF_6 is achieved by fractional distillation. It is expected that decontamination factors of 10^4 to 10^6 can be achieved by the fluorination–distillation step.

DECLADDING OF STAINLESS-STEEL- AND ZIRCALOY-CLAD UO_2 FUEL

Two methods are being investigated for decladding stainless-steel-clad UO_2 fuel elements: (1) oxidative decladding by reaction of UO_2 fuel pellets with oxygen to produce U_3O_8, which forms as a very fine powder and readily separates from the cladding, and (2) the chemical destruction of the cladding by the high-temperature reaction with oxygen in the presence of hydrogen fluoride.

Oxidation of UO_2 to U_3O_8 Powder

Processing of power-reactor fuels by low-decontamination methods has been investigated at Atomics International. One method under development for UO_2 fuels is based on the oxidation of the fuel in oxygen to remove the fuel

from the cladding as U_3O_8 powder and reduction of the higher oxide to UO_2 by hydrogen. Uranium dioxide fuels irradiated to burnups as great as 31,000 Mwd/ton have been declad by the oxidation process.[8] Decladding was carried out at 450°C in an atmosphere of oxygen at a pressure of 15 to 16 in. Hg. As the reaction between oxygen and UO_2 progressed, it was necessary to add oxygen periodically to maintain constant oxygen pressure. The final stages of the reaction were completed at a temperature of 600°C. Sections of fuel 3 to 4 in. long could be declad directly by this method; for longer sections of fuel, it was necessary to puncture the cladding at 1-in. intervals to assure high reaction rates and complete removal of the fuel from the cladding.[9] Periodic vibration of the fuel sections during oxidation was employed to provide continuous exposure of the unreacted fuel to oxygen. It was observed[9] that the expansion resulting from the oxidation of UO_2 to U_3O_8 produced sufficient force to cause the cladding to split along its entire length (see Fig. III-1). Mild agitation

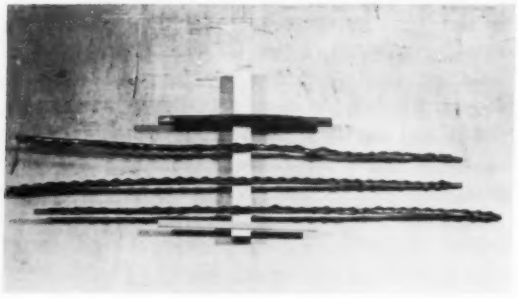

Fig. III-1 Stainless-steel cladding after UO_2 removal.[9]

caused the U_3O_8 product to separate completely from the cladding. The product from the decladding operation was 90 to 95% U_3O_8, and no contamination from the cladding was detected in the product by chemical analysis.

Decladding of Stainless Steel with HF–Oxygen

Workers at Brookhaven National Laboratory (BNL) have investigated the use of HF–oxygen mixtures to declad stainless-steel-clad UO_2 fuel.[10] A series of tests was performed in a 1.5-in.-diameter fluid-bed reactor to establish optimum reaction conditions. The tests were performed by immersing cylindrical specimens in a fluidized bed of refractory alumina particles. Maximum reaction rates at 600°C for type 348 stainless steel occurred at 40 vol.% HF in oxygen. The effect of temperature on the reaction rate in 40 vol.% HF–60 vol.% O_2 mixtures is shown in Fig. III-2. No significant

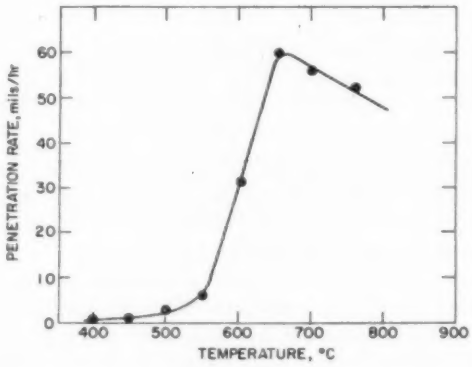

Fig. III-2 Penetration rate of type 348 stainless steel by 40% HF–60% O_2 mixture in a fluidized bed.[10]

reaction occurs at temperatures below 450°C; at temperatures above 550°C the reaction rate increases markedly to a maximum of 60 mils/hr at 650°C. The reaction rate decreases slightly at temperatures above 650°C.

Decladding of Stainless Steel with HF–Oxygen and Fluorination of UO_2F_2

Pilot-scale studies have been performed at ANL in a 3-in.-diameter fluid-bed reactor to demonstrate the destructive oxidation and fluorination of stainless-steel-clad UO_2 fuel.[1] A simulated fuel bundle (six 3-ft-long type 304 stainless-steel tubes containing 4.5 kg of cylindrical UO_2 pellets) was completely reacted in a 3-hr period at 550°C with a 40 vol.% HF–60 vol.% oxygen mixture. After destructive oxidation of the cladding, the fluid-bed material consisted mainly of alumina, alpha Fe_2O_3, and UO_2F_2 in the proportions 2.1 to 1 to 2.1. The UO_2F_2 was primarily in the form of fines (<325 mesh). The next step, fluorination, was conducted in two parts to facilitate the processing of a bed containing a large proportion of reactive fines. The bulk (~82%) of the uranium was recovered in a 6.5-hr period at 400°C with

dilute fluorine (10 vol.% fluorine in nitrogen) introduced at approximately the middle of the bed and with the main fluidizing gas stream (nitrogen) fed at the bottom of the reactor. This was followed by an 11-hr fluorination period at 450°C, with dilute fluorine being fed at the bottom of the column. The fluorine concentration was increased gradually from about 10 vol.% to a final value of 90 vol.%. A final concentration of uranium in the alumina bed of 0.05 wt.% indicated a recovery of about 99.9% of the uranium in the charge. The Fe_2O_3 material produced during decladding was entirely converted to FeF_3 fines in the fluorination step. The fluorine efficiency for the entire run, based on the reaction of fluorine with both UO_2F_2 and Fe_2O_3, was 67%. The bed at the end of the run was free-flowing, and no caked material was found in the bed.

Reaction of Zirconium and Zircaloy-2 with HF–Oxygen

Workers at BNL[10] have found that zirconium metal and Zircaloy-2 react rapidly with mixtures of hydrogen fluoride and oxygen. Results of tests performed in fluid-bed equipment indicate that maximum reaction rates for Zircaloy-2 occur at 625°C with a gaseous mixture containing 40 vol.% HF in oxygen (see Figs. III-3 and III-4). Analyses of the reaction product indicated that both ZrO_2 and ZrF_4 are formed. Apparently prolonged exposure to the HF–oxygen mixture resulted in the partial conversion of ZrO_2 to ZrF_4.

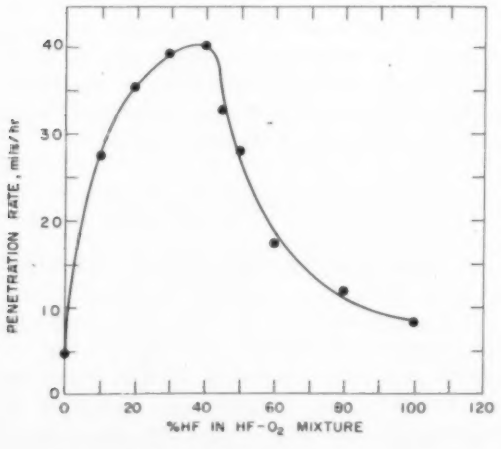

Fig. III-3 Effect of HF–O_2 concentration on penetration rate of Zircaloy-2 at 625°C in a fluidized bed.[10]

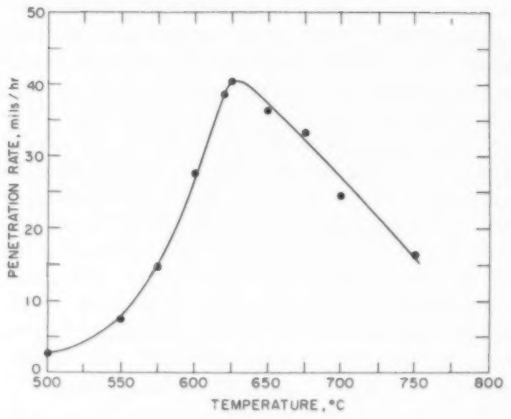

Fig. III-4 Effect of temperature on the penetration rate of Zircaloy-2 by 40% HF–60% O_2 mixture in a fluidized bed.[10]

RECOVERY OF PLUTONIUM FROM URANIUM DIOXIDE FUEL

In the fluid-bed fluoride-volatility process, declad fuel elements in a bed of alumina particles are reacted with oxygen to produce oxides, which are then treated with fluorine at 450 to 550°C to convert the oxides to volatile UF_6 and PuF_6 that are subsequently separated from each other and from fission products. Of major concern in the development of the process is defining the behavior of plutonium during the separation steps and establishing processing conditions that result in minimum retention of plutonium on the fluid-bed material after fluorination. A series of laboratory-scale fluorination experiments has been made at ANL[1] to determine the feasibility of decreasing the average plutonium retention for each batch by reusing the same alumina-bed material for the fluorination of several batches of feed material containing a mixture of U_3O_8, PuO_2, and fission-product oxides. (This oxide material represents the material resulting from a process step in which the sintered UO_2–PuO_2 fuel is converted to powder by reaction with oxygen.) In these experiments each addition of the oxide charge involved feeding 300 g of the mixed oxides into the alumina fluid bed at 450°C and fluorinating the mixture with 20 vol.% fluorine in nitrogen. This step was followed by recycle–fluorination periods of 5 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C, using 100% fluorine. In one series of experiments in which the fission-product

oxide mixture did not contain MoO_3, the plutonium level (0.0036 wt.%) in the alumina bed after the second addition–fluorination cycle corresponded to volatilization of 99% of the plutonium in the first two batches. After the seventh addition–fluorination cycle, the plutonium level was 0.0088 wt.%, corresponding to volatilization of 99.4% of the total plutonium fed. An eighth addition–fluorination cycle was performed after adding as much plutonium as in the previous seven cycles; the plutonium concentration of the alumina at the end of the cycle was 0.025 wt.%, corresponding to a cumulative volatilization of 99.2%. For a comparable series in which MoO_3 was present in the fission-product mixture, it was found that about seven cycles would be necessary to volatilize 99% of the plutonium.

A series of experiments has been made to determine the effect of the presence of iron oxides from the decladding of stainless steel on plutonium retention in the alumina bed. The fluidized-bed experiments were performed using fluorination periods at three temperature levels. In the first fluorination period, which was carried out at 450°C, the initial fluorine concentration in the gas phase was increased from 5 to 20 vol.% in nitrogen over a period of about 1 hr as the major part of the uranium was fluorinated. This was followed by recycle–fluorination periods of 4 hr at 450°C, 5 hr at 500°C, and 10 hr at 550°C using 100% fluorine. The results of these experiments showed that the plutonium concentration in the alumina bed was not significantly increased by the presence of iron oxides in the reaction mixture. On the basis of chromium analysis of the final bed, 30 to 40% of the chromium from the stainless-steel decladding product remained in the bed, and the remainder of the chromium volatilized.

OPERATIONS FOR SEPARATION OF URANIUM AND PLUTONIUM

Workers at ANL are investigating a method for effecting the separation of uranium from plutonium based on the selective fluorination of uranium with bromine pentafluoride.[11–14] In the first step of the conceptual process, the uranium in uranium–plutonium bearing fuel is fluorinated by BrF_5 to UF_6, which is volatilized from the reaction vessel and collected in a condenser along with excess BrF_5, the reaction product BrF_3, and volatile fission-product fluorides. During the conversion of uranium to UF_6, plutonium reacts to form nonvolatile PuF_4 and remains in the reaction vessel. The UF_6, interhalogens, and volatile fission-product fluorides are separated by fractional distillation, resulting in the production of decontaminated UF_6. The BrF_3 in the mixture of bromine fluorides is refluorinated to BrF_5, and the BrF_5 is recycled.

In a second fluorination step, the PuF_4 that remains in the reaction vessel is fluorinated with fluorine to PuF_6. The PuF_6 is collected in a series of separate cold traps. After collection the PuF_6 is revaporized and passed into a heated vessel where it is thermally decomposed to nonvolatile PuF_4.

A research program has been initiated to study the reactions between various uranium compounds and bromine pentafluoride. Recent work[12] has included studies of the kinetics for the UF_4–BrF_5 and UO_2F_2–BrF_5 reactions over the temperature range 175 to 300°C. The data were treated using a diminishing-sphere model in which F, the fraction reacted, is related to a rate constant k' and a reaction time t by the expression $(1-F)^{1/3} = 1-k't$.

Values of k' for the reaction of UF_4 with BrF_5 in the temperature range 175 to 275°C varied from 0.0005 to 0.0344 min^{-1}. The integrated form of the Arrhenius equation for the reaction rate constants is

$$\log k' = 5.7194 - 3948.3/T$$

The apparent activation energy for the reaction was calculated to be 18.1 kcal per mole of UF_4.

Values of k' for the reaction of UO_2F_2 with BrF_5 in the temperature range 175 to 300°C varied from 0.0040 to 0.0276 min^{-1}. The least-squares fit of the Arrhenius equation to these data established the following relation:

$$\log k' = 1.4931 - 1747.1/T$$

An apparent activation energy of 8.0 kcal per mole of UO_2F_2 was calculated for the reaction.

In experiments[12] performed to determine the comparative reactivities of BrF_5 and fluorine toward uranium compounds, it was shown that the reaction rate constants for reactions involving fluorine were lower by an order of magnitude than the rate constants for comparable reactions with BrF_5.

In laboratory tests performed in a horizontal tubular reactor, it was observed that high uranium recoveries from mixtures containing alumina, UF_4, UO_2F_2, and fission-product oxides can be achieved by the use of BrF_5 in relatively short exposure periods at modest temperatures.[14] Approximately 98% of the uranium was converted to UF_6 in 1 hr at 250°C with 20 vol.% BrF_5 in nitrogen. The presence of stainless-steel decladding product (formed by the action of HF–oxygen mixtures on stainless steel) does not appear to affect uranium removal.[14]

Plutonium is not volatilized during BrF_5 fluorination.[13] In a test in which a mixture of PuO_2, U_3O_8, and fission-product oxides was contacted for 1 hr at 400°C with a gas phase containing 20 vol.% BrF_5 in nitrogen, it was observed that the uranium was completely converted to UF_6 whereas no volatile plutonium species was formed. The plutonium in the residue was readily converted (99.5% conversion) to PuF_6 by reaction with fluorine for 8 hr at 550°C. The nonvolatile character of the plutonium product from BrF_5 treatment was verified in a separate test in which PuO_2 alone was reacted with BrF_5 for 1 hr at 400°C. The results of these tests indicate that quantitative separation of uranium and plutonium by selective fluorination with BrF_5 appears feasible.

FILTRATION OF HYDROLYZED PLUTONIUM HEXAFLUORIDE

High-efficiency cleaning systems for treating the environmental air in plutonium-handling facilities such as glove boxes are required since the permissible concentrations for plutonium in air are extremely low (3×10^{-8} mg of ^{239}Pu per cubic meter of air). Since particulate materials conveyed in the air are satisfactorily retained by high-efficiency AEC type filters that are employed in plutonium facilities, an investigation is being carried out at ANL[1,15–17] to determine those factors which affect the filtration of plutonium particulate matter obtained by the hydrolysis of PuF_6 with water vapor in the air. An understanding of the hydrolysis and filtration mechanisms is required in order to evaluate and design ventilation systems for plutonium service.

The reaction between PuF_6 and water vapor is believed to proceed as indicated by the following equation:

$$PuF_6(gas) + 2H_2O(gas) \rightarrow PuO_2F_2(solid) + 4HF(gas)$$

Examination of the solid hydrolysis product by X-ray diffraction confirmed[15] that the reaction product is PuO_2F_2, a homolog of the compound UO_2F_2 that is formed when UF_6 is hydrolyzed. Because of this similarity in behavior and the convenience of handling UF_6, UF_6 was used as a stand-in for PuF_6 in hydrolysis tests simulating the release of dilute PuF_6 into an atmosphere of moist air.[16,17] In experiments to determine the kinetics of the hydrolysis reaction, UF_6 in a dry gas was mixed with a wet gas and passed through a segmented packed bed of glass beads of known surface area and then through three AEC filter disks. Nitrogen was the diluent gas in this work. In all cases a large excess of moisture over that required for complex hydrolysis was present. A schematic diagram of the equipment is shown in Fig. III-5. The equipment permitted the removal of the packed bed in segments and also individual removal of the filter disks, each of which was analyzed separately for uranium content.

Hydrolysis rates were calculated for each packed-bed segment. The rates increased with increases in the partial pressure of either water or UF_6. Rates ranging from 0.3×10^{-4} to 0.1 mg of uranium per hour per square centimeter were obtained.

For the effects of partial pressures of UF_6, water, and HF to be defined more clearly, the experimental data were correlated by use of a semiempirical rate equation for reactions catalyzed by solid surfaces. The following rate equation was found to fit the experimental data from the dilute releases to within a standard deviation of 26%:

$$r = \frac{191.5\, p_{UF_6}\, p_{H_2O}}{1 + 597\, p_{UF_6} + 95.5\, p_{HF}}$$

where r is the reaction rate in milligrams of uranium per hour per square centimeter and p is the partial pressure of subscripted component at the solid surface in millimeters of mercury.

Preliminary data on the kinetics of PuF_6 hydrolysis have been obtained[1] in equipment identical to that used for studies with UF_6. Analysis of the results indicates that the rate

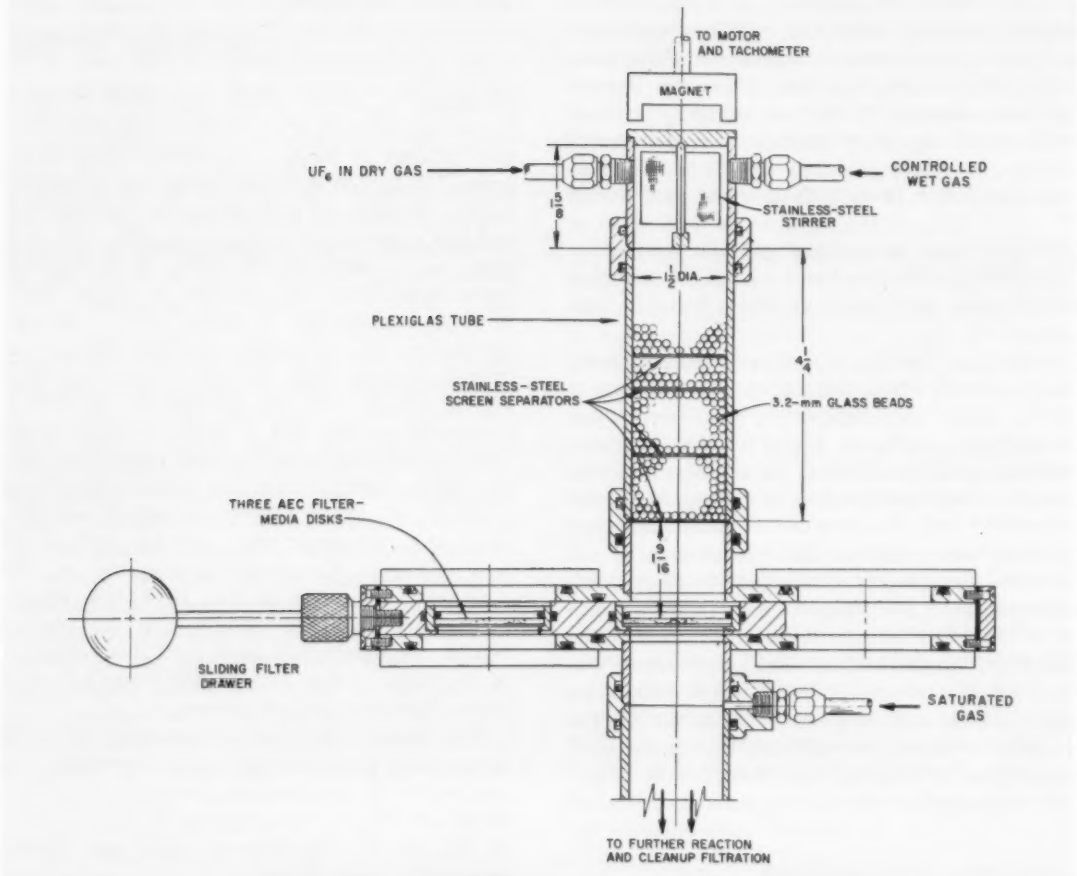

Fig. III-5 Uranium hexafluoride hydrolysis apparatus.[17]

of hydrolysis of PuF_6 is not more than twice, nor is it less than, the rate of hydrolysis of UF_6.

A series of three experiments has been performed to determine surface reaction kinetics for the hydrolysis of a mixture of PuF_6 and UF_6 in a gas stream.[18] Two air streams, one containing the mixed hexafluorides and the other containing moisture, were rapidly mixed and passed through a segmented bed of glass spheres. The quantities of plutonium and uranium retained on the glass spheres within the various bed segments were used to estimate rates of hydrolysis for UF_6 and PuF_6 in the mixture. The results showed that the rates of hydrolysis of the component hexafluorides in the mixture differed from the rates obtained when the hexafluorides were individually hydrolyzed. In experiments in which air of low moisture content (about 70 ppm) was used, the hydrolysis rates for PuF_6 in the mixture were markedly higher than rates obtained when PuF_6 alone was hydrolyzed. On the other hand, hydrolysis rates for UF_6 in the mixture were lower than rates obtained with UF_6 alone. In the mixed gas the hydrolysis rates for PuF_6 were always higher than the hydrolysis rates for UF_6. The data indicate that the hydrolysis mechanism for mixed hexafluorides is more complex than that expected on the basis of mechanisms for individual hexafluoride species.

An accidential release of 5.7 g of PuF_6 into a ventilated glove box occurred recently at ANL.[19] Although the release was accidental, it provided an excellent opportunity to study

the containment of PuF_6 in an alpha enclosure, especially since the glove box and the glove-box filters had not been previously exposed to plutonium. The ventilation air leaving the glove box was filtered by two banks of filters in parallel; each filter bank contained two AEC filters in series. The filtered air passed through a scrubber and then through the stack filter (two AEC filters in parallel) before discharge to the building exhaust system. The total quantity of plutonium discharged from the stack was estimated to be 2.6 μg. All attempts to detect plutonium at monitoring stations downwind from the release stack failed to show any plutonium above normal background levels.

The plutonium distribution throughout the filtering system was determined in order to evaluate the performance of the air cleanup system and to compare the performance with the results of small-scale release experiments that had been designed to simulate large-scale releases. It was determined that the fraction of plutonium which penetrated the AEC filters was within the range expected on the basis of results from small-scale release experiments.[20] As a result of study of the plutonium-distribution data, it became apparent that the performance of the filtering system could be improved by: (1) in-place testing of the filters after each change of filters to indicate the presence of any flaw in the filter media or in the gasket and (2) providing a separate gasket for each filter and a more positive means of effecting the seal in the installation of successive filters in the glove-box filtering system.

PROPERTIES OF PLUTONIUM HEXAFLUORIDE

The volatility of PuF_6 is utilized in the fluid-bed fluoride-volatility process to separate plutonium from most of the fission products. During the fluorination step and in subsequent operations, plutonium compounds are exposed to radiation from fission products. Steindler, Steidl, and Fischer[21] have studied the decomposition of PuF_6 by gamma radiation and have observed that the G value* for the decomposition to PuF_4 and fluorine was 7.5 ± 1.7. Details of this study were reviewed in the Winter 1964–1965 issue of *Reactor Fuel Processing*.[22]

*The number of molecules decomposed per 100 ev of absorbed radiation.

Plutonium hexafluoride decomposes by alpha radiation to PuF_4 and fluorine.[1] The results of a kinetic study of the decomposition of PuF_6 by alpha radiation have been published by Wagner and associates.[23] In tests performed at temperatures between 26 and 82°C, it was observed that the rate of decomposition is nonlinear, varying from 1.78 to 0.064%/day over the period of 0.5 to 571 days. Experiments with PuF_6 at initial pressures of 50 and 100 mm Hg showed that, at the lower pressure, slightly lower decomposition rates are obtained. The presence of helium or krypton lowers the rate slightly. Oxygen or fluorine decreases the PuF_6 decomposition rate, and nitrogen reacts slowly with PuF_6 to form NF_3. Increased nickel-surface area gives increased PuF_6 decomposition rates.

Reaction of Fluorine with Materials

Since fluorine gas is the primary agent employed in fluoride-volatility processes for the recovery of uranium and plutonium from nuclear reactor fuel materials, an understanding of the reactions of fluorine with various substances is important. Kuriakose and Margrave[24] have investigated the kinetics of the reaction of graphite and fluorine between 315 and 900°C. At temperatures between 315 and 530°C, graphite gains weight in fluorine linearly because of the formation of solid poly (carbon monofluoride) (C_xF_x); above 600°C, graphite loses weight with the formation of gaseous carbon fluorides. Between 530 and 600°C both modes of reaction occur. At all temperatures in the range studied, the reaction rate is proportional to the fluorine partial pressure. An activation energy of 42.5 kcal/mole was calculated for the reaction forming poly(carbon monofluoride) between 315 and 400°C, and dissociation of fluorine on the graphite surface is believed to be the rate-determining step in this process.

The kinetics and mechanism of the reaction of fluorine with copper(I) oxide and copper(II) oxide have been investigated by Ritter.[25] The reaction of fluorine with CuO was found to take place by a diffusion-controlled mechanism at temperatures between 82 and 151°C and at fluorine pressures between 40 and 80 mm Hg. An activation energy of 16.3 kcal/mole was calculated for the reaction. In the pressure range investigated, the reaction rate was pro-

portional to the square root of the fluorine pressure.

The reaction of fluorine with Cu_2O was found to occur by a two-step mechanism:

$$Cu_2O + F_2 \rightarrow CuF_2 + CuO$$

$$CuO + F_2 \rightarrow CuF_2 + 0.5O_2$$

The initial reaction in this two-step mechanism apparently exhibits linear reaction kinetics in the temperature range of 152 to 207°C and at fluorine pressures between 50 and 800 mm Hg. The activation energy for the reaction was 19.7 kcal/mole. It was observed that the reaction rate was proportional to the 0.63 power of the fluorine pressure.

In a study of the reaction between fluorine and copper at 450°C, O'Donnell and Spakowski[26] observed that the reaction was pressure-dependent and followed a logarithmic rate law. Since the rate data were best described by a logarithmic rate law, the authors suggest that the rate-controlling mechanism cannot be entirely attributed to diffusion of fluorine through the copper fluoride film.

Compact Pyrochemical Processes

By L. Burris and G. A. Bennett

Compact pyrochemical processes are nonaqueous processes for the recovery and purification of partially burned reactor fuels. They possess utility for the recovery of ceramic fuels (such as oxides or carbides) as well as metallic fuels and may be used in small plants serving one or several reactors. In general, these processes utilize molten-metal and molten-salt systems as processing media. The metal solvent systems consist principally of various binary alloys of magnesium with zinc, cadmium, and copper. The salt systems are halide salts of alkali and alkaline-earth metals. It is also possible to process both ceramic and metallic fuels directly, i.e., without dissolution in any solvent media.

These processes possess features which should be economically beneficial, particularly in fast reactor fuel cycles. Among these features are: (1) the ability to process short-cooled high-burnup fuels of both ceramic and metallic types with consequent reductions in fuel inventory, (2) the decrease in criticality problems because of the absence of aqueous solutions, (3) the recovery of expensive alloying agents, and (4) the direct production of concentrated fission-product wastes.

EBR-II Fuel Cycle Facility and Operations

On Sept. 13, 1965, the Experimental Breeder Reactor No. 2 (EBR-II) and the adjacent Fuel Cycle Facility, located at the National Reactor Testing Station in Idaho, were dedicated in a short ceremony.[27] This dedication formally recognized the successful construction and operation of this unique experimental complex, which has now demonstrated the practicality of the closed fuel-cycle concept, i.e., the purification of spent fuel elements in a plant adjacent to the reactor and their subsequent refabrication and recharging into a reactor core.

The closed fuel cycle in operation at the EBR-II site is well known.[28] In this cycle the partially spent fuel, after removal from the reactor subassemblies, is decontaminated by a compact pyrochemical process, melt refining,[29] and subsequently refabricated into pins, which are then incorporated into new fuel subassemblies for return to the reactor. The residue from melt refining (5 to 10% of the charge) will be purified by the skull-reclamation process,[28,29] which is currently under full-scale development at ANL.[30] A blanket process, to isolate the bred plutonium from the EBR-II blanket, is also being developed.[28,30]

The melt-refining process[28] has continued to operate satisfactorily. In this process, spent uranium fuel pins from the EBR-II reactor are partially decontaminated from their fission products: Certain fission products such as the noble gases volatilize, and other fission products such as the rare earths are selectively oxidized by reaction with a lime-stabilized zirconia crucible at 1400°C for about 3 hr.*

*The oxidized fission products, a small amount of oxidized uranium, and some unpoured uranium are retained as a residue, or skull, in the crucible after the purified metal is poured. Since this material constitutes 5 to 10% of the uranium in the charge, the skull must be processed further to recover the uranium. This further processing is known as the skull-reclamation process. The current status of this process is discussed in this issue of *Reactor Fuel Processing*.

Pouring yields[31] obtained after nine melt-refining runs with irradiated fuel (material that had not been previously reprocessed) ranged from 92.7 to 94.5%.

The other operations necessary to complete the closed fuel cycle, namely, injection casting, pin processing, fuel-element assembly, welding, and bonding, all of which must be done remotely, are proceeding satisfactorily.[29]

EBR-II Skull-Reclamation Process

The skull-reclamation process is being developed at ANL specifically for the recovery of the 5 to 10% of uranium charge that is left in the melt-refining crucible as oxidized skull. The chemistry and technology developed in this process will also be applicable to the processing of a variety of uranium-bearing fuels, such as oxides, carbides, and metals.

This process, which has recently undergone modification,[29,32] begins with oxidation of the skull material and is followed by extraction of the relatively noble fission products into zinc from a suspension of the skull oxides in a halide flux. The zinc phase is then discarded to waste. The uranium oxides are then reduced by magnesium contained in a 60 wt.% magnesium–zinc reducing solution. Uranium metal precipitates almost completely out of the reducing solution. Rare-earth and alkaline-earth elements remain in the flux and supernatant metal phases, which are removed and discarded. The precipitated uranium is dissolved in a zinc–14 wt.% magnesium solution, and the product solution is transferred to the retorting operation. This revised process has been demonstrated in pilot-plant runs and is currently being tested at Argonne in plant-scale equipment (~4.25 kg of uranium per batch) for later installation in the EBR-II Fuel Cycle Facility.

Plant-Scale Development

Four plant-size runs following the modified flow sheet have been completed in the skull-reclamation furnace,[33] which operates at temperatures between 700 and 810°C. The elapsed operating time for a run using this flow sheet is about 10 hr as compared to about 18 hr for the previous flow sheet.[34] No difficulties were encountered in carrying out any of the mechanical operations; these included charging of materials, heating, mixing, sampling, and transferring molten metal and fluxes from the furnace to exterior receivers.

During these runs some twenty trouble-free transfers of waste-metal supernatants, waste fluxes, and product solutions were accomplished through the recently rebuilt transfer line.[33] This rebuilt transfer line consists of a ½-in.-ID molybdenum–30 wt.% tungsten tube heated by a silica-insulated Chromel P wire wound around the tube.

Retorting is utilized to recover the uranium from the uranium-product solution produced in the dissolution step of the skull-reclamation process. In the retorting step the magnesium–zinc–uranium ingot from the skull-reclamation furnace is transferred to a large BeO crucible (8½ in. in outside diameter by 17 in. in overall height by ½ in. in wall thickness). The magnesium–zinc is then distilled at 800 to 900°C from the uranium-product solution, after which the uranium is melted (~1200°C) to form an ingot. Two preliminary runs using the same BeO crucible (a thixotropically cast crucible) were completed in plant-scale retorting apparatus located in an inert-atmosphere enclosure. The charge in each run consisted of a zinc–13.5 wt.% magnesium (no uranium) ingot weighing about 38 kg. This quantity of zinc–magnesium would normally be associated with about 4.25 kg of uranium product. Overall performance and apparent distillation rate of the equipment were satisfactory. After these two runs the BeO crucible was in excellent condition. In future runs, feed charges to the BeO crucible will contain uranium.[33]

Pilot-Plant-Scale Development

Seven pilot-plant demonstration runs (1.5 kg of uranium) of the skull-reclamation process[33] using the modified flow sheet were completed before the runs were discontinued in June 1965. Chemical analyses of samples from four of the runs have shown that the noble-metal extractions were identical with those of earlier runs. Good removals of ruthenium (~80%) were accomplished; molybdenum removals continued to be barely adequate. The data suggest that incomplete reduction of the molybdenum in the noble-metal-extraction step is the probable cause for poor molybdenum extraction.[33] The reason for the incomplete reduction is uncertain. Because further molybdenum removal is possible during the product-dissolution step,

it is believed that overall removals of molybdenum will be satisfactory.

Processes for Advanced Reactor Fuels

Compact pyrochemical processes are under development for processing uranium and plutonium oxide, carbide, or metallic cores and blanket material from fast breeder reactors. In the type of process under development at ANL,[31-35] molten-metal and molten-salt solvent media are employed. Fission products are separated from fissionable and fertile elements by selective oxidation and reduction reactions and subsequent favorable distribution of solute elements between molten-metal and molten-salt phases. At Atomics International, solvent-free processes[3,36-41] have been developed, primarily for the purpose of demonstrating low-decontamination methods for reprocessing reactor fuels of the ceramic type. These Atomics International processes usually oxidize directly by means of oxygen, carbon dioxide, or nitrogen, and reduce with hydrogen or carbon; separations of fission products occur by volatilization.

SALT–METAL PROCESSES

One type of salt–metal flow sheet which is being investigated at Argonne[33] is based on the selective transport of uranium and plutonium from a copper–magnesium solvent alloy to appropriate zinc–magnesium alloys through a salt phase consisting of a mixture of $MgCl_2$, NaCl, and KCl. The flow sheet involves first an oxidative decladding operation in which oxide fuels would be released from cladding. Carbide and metal fuels would be converted to oxides in this step. These are then reduced in a magnesium–10 wt.% copper alloy. The highly electropositive fission elements, alkali, rare-earth, and alkaline-earth elements, distribute strongly to the $MgCl_2$–NaCl–KCl salt phase and are removed in it. Then, if advantage is taken of their widely different solubilities and their different distribution coefficients in the solvent systems, the uranium and plutonium can be separated by selective transfer through a salt phase to separate metal phases such as zinc–5 wt.% magnesium.* Transfer of uranium and plutonium could be done successively or simultaneously.

Copper–Magnesium and Zinc–Magnesium Solvents

The possibility of effecting a separation of uranium from zirconium using copper–magnesium and zinc–magnesium solvents in mutual contact with a molten salt was investigated experimentally. With both uranium and zirconium initially present in the copper–magnesium alloy, copper–8 wt.% magnesium and zinc–5 wt.% magnesium were equilibrated in mutual contact with molten $MgCl_2$ at 770°C. It was found that 83.4% of the uranium transferred to zinc–magnesium alloy whereas 99.2% of the zirconium remained in the copper–magnesium alloy. Although the uranium recovery and the rate of transfer in this experiment were not adequate for process use, it is believed that these problems can be overcome by appropriate equipment design and choice of conditions. If so, this system should provide a much better uranium–zirconium separation than any other liquid-metal process investigated thus far. In this separation scheme, noble-metal fission products, as well as zirconium, are separated from uranium.

A supporting program to find an inexpensive, easily fabricated construction material for this process is in progress. Four ferrous alloys[31] (304 stainless steel, 405 stainless steel, AISI 4130, and AISI 1020) were exposed to three copper–magnesium solutions (50 wt.% copper–magnesium, 70 wt.% copper–magnesium, 90 wt.% copper–magnesium) at 600 and 800°C for 200 hr in the presence of purified halide salt ($MgCl_2$–NaCl–KCl). The results obtained show little corrosion in any combination at 600°C; at 800°C the corrosion increased significantly, the higher corrosion rates occurring with increased concentration of copper in the melt. However, even at 800°C the corrosion was sufficiently low (<2.0 mils in 200 hr) to warrant further testing. Consequently the solubility of iron in liquid copper–magnesium alloys was determined. The values were low,[33] ranging from 0.14 wt.% iron in copper–9.0 wt.% magnesium at 850°C down to 0.0115 wt.% iron in copper–33.5 wt.% magnesium at 600°C. These low solubility values are consistent with the low corrosion rates that have been observed. Further, at these low concentrations, iron should have no adverse effect on the process.

*The application to fuel processing of solute transfer between liquid alloys in mutual contact with a molten salt has been discussed by Chiotti and Klepfer.[42]

In connection with the use of zinc–magnesium alloys as process solvents, the solubility of plutonium in this system is of interest.[31] Solubility data were obtained at 600, 700, and 800°C from analyses of filtered samples of liquid zinc–magnesium alloys saturated with plutonium. Although the liquidus lines and the phase diagram of this ternary system are still tentative, a liquid-miscibility gap in the magnesium-rich composition region has been observed. This would be expected because of the similar miscibility gap previously observed in the binary plutonium–magnesium system.[43]

Since zinc–magnesium alloys are used in various liquid-metal processes, solubilities of container-material constituents and fission products in these alloys and their constituent elements are of interest. The following solubilities of iron, niobium, zirconium, and chromium at 800°C were obtained during measurements of distribution coefficients:[34]

	Solubility (wt.%) in		
	100 wt.% Zn	50 wt.% Zn–50 wt.% Mg	100 wt.% Mg
Iron	7.7	0.2	0.075
Niobium	3.0	0.04	<0.0001
Zirconium	12	0.95	0.64
Chromium	1.5	0.08	~0.045

This table suggests that conventional materials may possibly be used in processes in which the solvent metals are high in magnesium and low in zinc; further, the wide variations in solubilities may be advantageous in the development of purification processes.

Cadmium-Base Solvents

In another general type of process, also under development at Argonne,[34] cadmium-based solvents are employed for the recovery and purification of uranium–plutonium fuels by liquid-metal–molten-salt extraction procedures. Multistage countercurrent extraction, either batch or continuous, is required to achieve adequate recovery and purification of uranium and plutonium. Two systems are being considered for use as the liquid-metal phase: 85 at.% cadmium–15 at.% magnesium, and 70 at.% cadmium–15 at.% magnesium–15 at.% zinc.* Information on solubilities of plutonium, uranium, and fission products in process solvents, corrosion of candidate materials of construction, stability of uranium and plutonium solutions, distribution coefficients of fuel constituents between liquid metals and molten salts, and other physical properties of pertinent systems is being reviewed and extended to determine which of the two solvents should be selected for further process-development studies.[34]

Engineering work related to the development of continuous molten-metal–molten-salt extraction processes is under way. Initial experiments were designed to permit examination of metal–salt extraction kinetics for transient reactions in packed columns.[32] In these experiments a metal alloy of cadmium–11 wt.% zinc–5 wt.% magnesium containing uranium or cerium was passed through a packed quartz tube filled with static, molten salt (50 mole% $MgCl_2$–30 mole% NaCl–20 mole% KCl). These transient tests have indicated that equilibrium stage heights of less than 2 ft can be expected in packed columns. The tests have also indicated the order of magnitude of typical mass transfer rates and thus have demonstrated the feasibility of countercurrent extractions in the system.

An engineering-scale facility has been constructed at Argonne for purification of large batches (50 kg) of molten chloride ($MgCl_2$–NaCl–KCl) salt.[34] Untreated salts containing $MgCl_2$ are extremely corrosive toward all steels because of the presence of large quantities of insolubles and substances, particularly water, that react with UCl_3 to release corrosive gases such as chlorine and HCl. The impure chloride-salt mixture is purified by contacting it with a cadmium–magnesium alloy at 550 to 600°C and then filtering at temperatures between 450 and 500°C through a stainless-steel filter having 20-μ pores. Four batches of salt have been purified in this facility. The quality of the purified salt, as measured by the content of oxygen and water-insolubles, has been progressively improving from batch to batch; analysis of the fourth batch indicated the presence of less than 0.1 wt.% oxygen and about 30 ppm water.[44]

*The zinc was added to increase uranium solubility; however, corrosion with this solvent system should be greater than with the zinc-free system.

SALT-CYCLE PROCESS

McKee[45] of Battelle–Northwest has presented the results of an investigation of the relative fuel-cycle costs of two alternative reactor fuel cycles employing light-water-moderated reactors and either central-plant or close-coupled-plant reprocessing and refabrication. The results are reviewed in Sec. I of this issue of *Reactor Fuel Processing*.

DRY PROCESSES

As stated earlier, Atomics International processes usually are based on direct oxidation of the reactor fuel, followed by direct reduction without the use of either solvent metals or salts. Two summary reports,[9,36] one applying specifically to carbide fuels and the other to oxide fuels, have recently been published. Other reports, which deal more fully with specific portions of these development programs, are also available.[37–40] These are phase-out reports, since all reprocessing studies at Atomics International are being discontinued.[16]

Oxide-Fuel Processing

One of the summary reports is that of Brand and Murbach[9] on the pyrochemical reprocessing of UO_2 by the AIROX (Atomics International Reduction Oxidation) process. This process is based on the oxidation of UO_2 fuel to U_3O_8 by oxygen and reconversion to UO_2 by reduction with hydrogen. Although the primary purpose of AIROX reprocessing is the preparation of recycle fuel, some fission products are removed during oxidation–reduction.

The following observations and conclusions relative to the process have been made:

1. Three-foot sections of stainless-steel-clad UO_2 were effectively declad by piercing the cladding at 1-in. intervals and exposing to oxygen at about 400°C. Uranium oxide carried through three oxidation–reduction cycles was pressed and sintered at 1700°C. Pellets having more than 98% of the theoretical density were produced.

2. Repeated oxidation–reduction effectively pulverizes the UO_2.

3. Kilogram-scale experiments, using uranium oxide and oxides of stable isotopes of representative fission products simulating burnups up to 100,000 Mwd per metric ton of uranium showed no significant physical or chemical effect of these elements on the process.

4. A multicycle experiment using remote methods demonstrated this process on the 100-g scale with irradiated fuel. Material irradiated to 21,000 Mwd per metric ton of uranium was declad, oxidized, and reduced through three cycles, pressed into pellets, sintered at 1700°C, reirradiated to an additional 10,000 Mwd per metric ton of uranium and the process repeated. Final pellet densities were from 94 to 96% of the theoretical density.

5. Cesium, rare gases, and iodine were virtually completely removed. Tellurium was partially removed, and ruthenium could be removed by carrying out one oxidation step above 725°C. No removal of rare earths was detected.

6. Fuel-cycle cost studies on UO_2 fuel, carried out for a 1000-Mw(e) complex (three boiling-water reactors),[46] indicate an economic advantage for AIROX, as compared to aqueous reprocessing. The ^{235}U inventory and burnup requirements are higher for the AIROX process than for aqueous reprocessing, but the resultant savings from a simpler process more than offset the higher burnup costs (estimated savings, ~0.2 mill/kw-hr).

Carbide-Fuel Processing

A similar summary report on the pyrochemical reprocessing of carbide fuels has also been presented by Murbach and Brand.[36] During this work three processes were investigated: the CARBOX process, a nitride–carbide process; and a fused-salt electrolysis process.

1. The CARBOX process, which is based on oxidation–carbothermic reduction. In this process the uranium carbide is reacted directly with oxygen, air, or carbon dioxide, followed by reaction of the oxide product with carbon to regenerate the uranium monocarbide. Although the oxidation behavior of UC is dependent on its previous history, ignition occurs at about 300°C in oxygen, 350°C in air, and at 525°C in CO_2. Oxidation was carried out on a laboratory scale, in 10-kg batches, and on irradiated material. Reduction was accomplished by carbon, using a graphite container, at temperatures of 1300°C and higher.

Some of the experiments conducted during the development of the CARBOX process have been reported in greater detail. Specifically, Smiley[37] has presented data and calculations on the evaporating of plutonium and fission products during the oxidation–reduction reprocessing of uranium carbide reactor fuel. He reported gram-scale experiments on the (1) reduction of tracer-irradiated UO_2 in a graphite crucible, (2) reduction of a uranium–cerium–samarium–neodymium oxide mixture in a tantalum effusion cell, (3) a reduction of a uranium–cerium oxide in a stream of helium, and (4) arc melting of tracer-irradiated UC. The results indicate that evaporation of plutonium is controlled by the equilibrium pressure, which is proportional to concentration and at least roughly in agreement with Raoult's law. Cerium behaved in a manner similar to that of plutonium. Evaporation of neodymium was similar to that of cerium, but removal of samarium was proportionately very much larger.

Calculations of the plutonium losses to be expected in typical production-scale operations indicate that the loss in the reduction should not be serious, except possibly by deposition on the crucible walls; this possibility should be investigated further. Losses of plutonium in arc-casting the carbide would almost certainly be substantial because of the high temperatures required. Therefore this method of refabrication cannot be used in any fuel cycle that recycles plutonium. The use of additives, such as nickel, to prepare dense UC at a maximum temperature of 1250°C has shown promise.[36] Further work on a larger scale and at higher burnup is recommended.

Strausberg[40] discussed the evaluation of a stainless-steel rotary kiln for the controlled oxidation of UC. The kiln, which is 16 in. in diameter by 21 in. long, was rotated at 8 to 10 rpm. Oxidation was monitored by measurement of the temperature of the charge and the CO_2 concentration in the off-gas. The kiln performed satisfactorily. Several 10-kg batches were oxidized at a rate of 2 to $2\frac{1}{2}$ kg/hr at 400 to 500°C. When the starting material was reactive UC, over 95% of the product was −200-mesh U_3O_8. This material is considered suitable feed material for reconversion to UC.

2. A nitride–carbide cycle, in which UC is converted to a nitride and then reconverted to the carbide. In this process the UC is heated in a nitrogen atmosphere at 800 to 950°C, and a mixture of uranium nitride and carbon is thus formed. The carbide is then re-formed by heating the resulting mixture to elevated temperature (>1600°C) in vacuum and is refabricated by arc melting or other means.

Rates for the reactions between UC and air, oxygen, carbon dioxide, and nitrogen are dependent on the chemical reactivity of uranium carbide, which Murbach[39] found to be a function of its previous treatment. Freshly arc-melted uranium carbide is relatively unreactive toward oxygen, nitrogen, and CO_2. After exposure to laboratory air for a few days, the material becomes reactive. This exposure is accompanied by an increase in apparent surface area of the order of 100 cm^2/g. It is postulated that the increase in surface is caused by hydrolysis along grain boundaries and that this increase in surface area causes the enhanced reaction rates.

3. A fused-salt electrolysis process, in which uranium carbide is anodized in fused LiCl–KCl eutectic containing UCl_3 to give deposits of uranium and uranium intermetallic compounds in liquid-metal cathodes. The uranium cathode deposit is removed from the salt, dissolved in hot mercury, and converted to UC by reaction with propane in mercury at 350 to 600°C. The mercury is removed by vaporization.

The cathode current efficiencies, as reported by Iverson and Sullivan,[38] decreased in the following order: lead, zinc, bismuth, and cadmium. The efficiencies ranged from 0.1 to 91%. The anode efficiencies varied in approximately the same manner and ranged from 1 to 93%. Under similar conditions, uranium anodes gave higher yields than uranium carbide anodes, and this difference was attributed to a greater loss of current through U^{3+}/U^{4+} cycling with uranium carbide anodes. The current efficiency decreased markedly with the increase in UCl_3 beyond an optimum concentration. This decrease in yield was attributed to a greater current loss through U^{3+}/U^{4+} cycling at higher UCl_3 concentrations.

Decontamination by all three processes was studied with lightly irradiated UC (integrated neutron flux $\sim 10^{17}$ neutrons/cm^2). The CARBOX and nitride processes remove about 75% of the fission products, but plutonium losses are high because of evaporation. The electrolysis process removes most of the fission products other than zirconium.

Cost studies on the CARBOX process indicate a potential savings of 0.1 to 0.2 mill/kw-hr when compared to conventional solvent extraction. No cost analyses have been reported for other processes.

Miscellaneous

German and British patents[47,48] were recently granted to Erler, Peray, and Petit (assigned to Commissariat à l'Énergie Atomique) based on the work reported at the XVIIIth International Congress of Pure and Applied Chemistry[49] in Montreal in August 1961. In this decontamination process the molten contaminated metal is contacted with oxide-containing cinders, which have a lower melting point than the uranium. The uranium is melted below the surface of the cinder, which is composed of a eutectic mixture of beryllium oxide and an oxide of at least one of the elements barium, calcium, strontium, magnesium, lithium, and lanthanum. The system is cooled to a temperature between the melting points of the cinder and the uranium, and the solid refined uranium is separated from the fluid cinder. An arc furnace for carrying out this process is described.

A survey of the advantages and disadvantages of pyrochemical processing was presented by D'hoht.[50] He reported on dry-processing investigations which were made to avoid difficulties that arise in wet processing of irradiated fuel.

Patents were also issued to Teitel and assigned to Dow Chemical Co. on methods of processing impure uranium.[51,52] The methods involve heating the uranium with copper, copper–aluminum, or copper–magnesium alloy, heating until the solvent metal becomes miscible with the uranium, and adding sufficient magnesium to cause precipitation of a uranium-containing solid. The uranium may then be recovered by phase separation and retorting.

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Section

IV

Reactor Fuel Processing

Waste Disposal

By P. Fineman

Treatment of Low- and Intermediate-Level-Activity Wastes

Ion Exchange

At the Idaho Chemical Processing Plant (ICPP), a quantity of various irradiated fuel elements are stored underwater in a fuel-storage basin.[1] The basin water consists of raw water with added chlorine (a residual concentration of 0.5 ppm) to inhibit growth of microorganisms and with added sodium nitrate (200 ppm) to control corrosion; the *p*H of the basin water is 8.2. The principal radioactive contaminants are ^{90}Sr ($\sim 3.5 \times 10^{-4}$ to 10×10^{-4} $\mu c/ml$) and ^{137}Cs ($\sim 0.8 \times 10^{-3}$ to 1.3×10^{-3} $\mu c/ml$). For corrosion-control purposes, 100,000 gal of basin water is removed each month. However, before the basin effluent is released to the environs, it is passed through ion-exchange columns containing clinoptilolite[1,2] for removal of the ^{90}Sr and ^{137}Cs. The exchanger is used on a once-through basis until it is exhausted; the column with its contents is removed from the system, sealed, and then buried as a solid radioactive waste.

The ion-exchange system[1] consists of four columns in parallel; each column is made up of two 55-gal carbon-steel drums connected in series. Each drum contains a 24-in.-deep bed of clinoptilolite (0.25- to 2.0-mm-diameter particles); for the two drums in series, this represents an effective exchanger length of about 48 in.

A single unit consisting of two drums in series is shown in Fig. IV-1. In the loading cycle the basin water is fed to the drum at the top of each column. The piping is arranged to maintain each drum about one-half full of water. In addition, a siphon-break loop for each drum extends from the drain line up above the drum, then returns to the drum, and terminates with the open end of the siphon break just below the lip.

In operation, all the cesium is retained in the top drum; the strontium is retained in both drums. The bottom drum, when exhausted, is drained of excess fluid and is then used to replace the top drum. The top drum is then sealed for disposal; its usual radiation level is about 2 r/hr at 1 in.

In a 13-month operating period, this ion-exchange system was successfully used for the

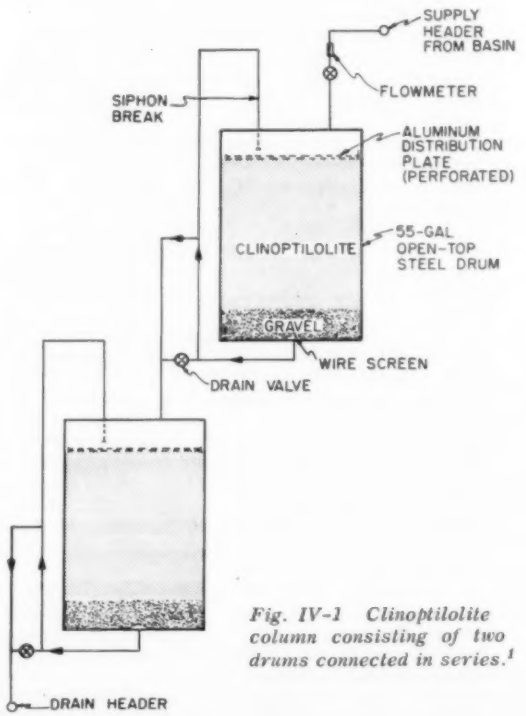


Fig. IV-1 Clinoptilolite column consisting of two drums connected in series.[1]

decontamination of some 1,300,000 gal of basin water; approximately 24 cu ft of clinoptilolite was used. Analyses for cesium and strontium in the treated effluent showed that the cesium concentration was well below drinking-water tolerance and that the average strontium concentration was near drinking-water tolerance. When the treated effluent is discharged to the environs, additional strontium decontamination and dilution do occur. Additional strontium is sorbed as the effluent percolates through the soil, and dilution occurs when the effluent reaches the groundwater aquifer. It is noted, however, that soil sorption and groundwater dilution are considered only as secondary safety measures.

Decontamination of Purex-Plant Wastes at Pacific Northwest Laboratory

At Pacific Northwest Laboratory (PNL), a pilot-plant study[3–5] of the ion-exchange treatment of Purex tank-farm alkaline condensate is being carried out. The treatment of the condensate, an intermediate-level-activity waste, consists of the following steps:

1. Steam stripping of the condensate for bulk removal of ammonium ion and organic material.
2. Filtration of the cooled bottoms from the stripping tower for solids removal and cesium decontamination. The filter contains a precoat of crushed clinoptilolite, which is a cesium-selective adsorbent.
3. Ion-exchange adsorption of the filter effluent for fission-product decontamination. The effluent is passed through a two-bed ion-exchange system consisting of an anion bed followed by a cation bed.

It was previously reported in this Review[3] that solids in the feed stream caused excessive pressure drops in the precoat filter and the anion-exchange column and that the chemical composition and behavior of the solids suggested that they were primarily organic and contained high concentrations of bacteria. For the pilot-plant study now in progress, a horizontal plate filter was installed to demonstrate its utility for solids removal and radionuclide sorption.[4] The filter area can be varied from a minimum of 0.9 sq ft to a maximum of 6.48 sq ft, depending upon the number of filter plates used.

One pilot-plant run was completed with actual plant-level-activity condensate containing added calcium hypochlorite for bacterial control.[5] The steam-stripped condensate was passed first through the precoated (clinoptilolite) filter and then successively through the anion column and the cation column. The filter effectively removed the particulate matter from the feed stream. The two-bed ion-exchange system performed very satisfactorily. In the effluent from the cation column, all radionuclides, except for ^{106}Ru, were less than their respective maximum permissible concentration for water (MPC_w); the ^{106}Ru amounted to 1.8 MPC_w. The ^{106}Ru breakthrough occurred after 100 bed volumes of filter effluent had passed through the anion exchanger; it also coincided with chloride-ion breakthrough. Since nearly all the chloride is introduced by the addition of calcium hypochlorite, anion-bed performance is expected to be improved under plant conditions where calcium hypochlorite or chlorine treatment would not be necessary.

Ion-Exchange Treatment of Harwell-Plant Waste

Workers[6] at Harwell have reported on a pilot-plant (500 gal/hr) demonstration of an ion-exchange process for the treatment of an intermediate-level-activity Harwell-plant waste. The flow sheet for the pilot plant is shown in Fig. IV-2. Two pairs of ion-exchange columns are used in the process and are operated in series; each pair consists of a strongly acidic polystyrene cation exchanger and a weak-base polystyrene anion exchanger. The ion-exchange columns are $8\frac{1}{2}$ ft high and 2 ft in diameter; the resin bed depth in each column is 4.3 ft. The feed is prefiltered[7] and then passed through the four ion exchangers in the following order: cation, anion, cation, and anion. Conductivity measurements of the effluent from the second pair of columns are used to indicate the demineralizing efficiency of the plant and to give an early warning of activity breakthrough. (Previous laboratory work[8] had shown that a sharp rise in conductivity occurs before activity breakthrough.)

Optimum use of ion-exchange capacity is achieved by operating the pairs of columns as follows: Only the first pair of columns is regenerated after breakthrough of the second pair of columns has occurred. Thus the original second pair becomes the lead pair through which the filtered feed is first passed, and the regenerated first pair becomes the second pair. A split regenerant scheme together with reuse of rinse waters is being used to reduce the volume of wastes produced in the regeneration

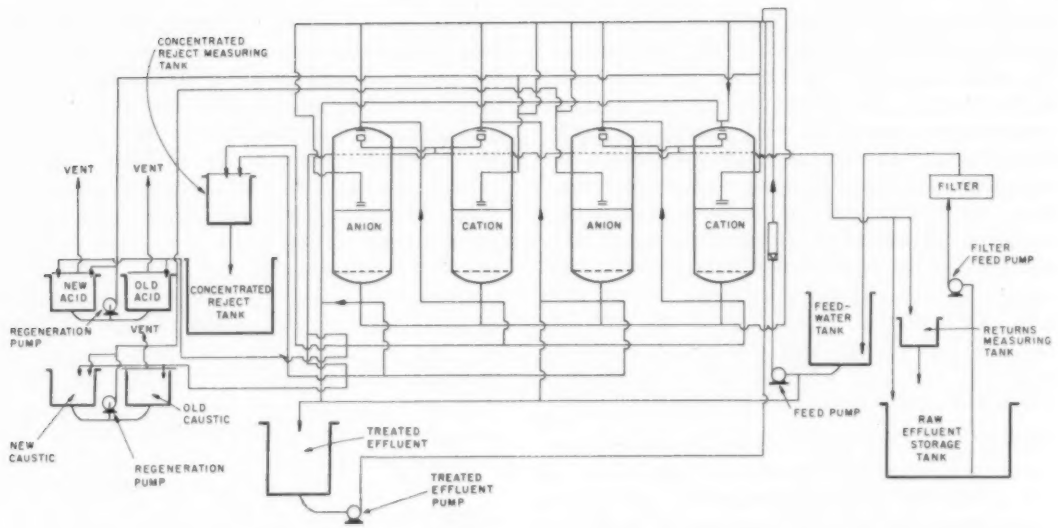


Fig. IV-2 Flow sheet of ion-exchange plant for treatment of Harwell-plant waste.[6] (Reproduced by permission of the U. K. Atomic Energy Authority from British Report AERE-R-4905.)

step. Each resin uses two bed volumes of regenerant solution: 4.4*N* nitric acid for the cation exchanger and 3.0*N* sodium hydroxide for the anion exchanger. However, the first of the two bed volumes of regenerant consists of previously used regenerant, and the second comprises fresh regenerant.

Some 227,000 gal of actual plant intermediate-level-activity waste was treated in the demonstration run. The waste contained the following principal nonradioactive cations and anions: sodium, calcium, magnesium, potassium, bicarbonates, chlorides, nitrates, and sulfates. Of the alpha and beta emitters present, the beta emitters represented the major portion of the two activities. Cesium and strontium accounted for 70% of the total beta activity.

The results of the ion-exchange treatment of the plant waste were as follows: The average decontamination factors were 1000 for alpha activity and 1250 for beta activity. The split regenerant scheme proved to be a satisfactory method for reducing the waste regenerant volume. The total volume of waste produced, including that of the prefiltration step, amounted to about 2% of the throughput.

Freeze Drying

The European Atomic Energy Community (Euratom)[9] has granted Leybold-Hoch-Vakuum-Anlagen G.m.b.H., Cologne, Germany, a research contract to develop a freeze-drying process[10] for the treatment of radioactive wastes. The process would produce an end product in the form of a powder that would be stored in metal containers.[9] An experimental processing plant will be built. It will be designed for a daily (24-hr) waste throughput of 100 to 400 liters (depending on solids content) and for handling an end product having a maximum radioactivity content of 1 curie/liter.

Conversion of High-Level-Activity Wastes to Solids

Fluid-Bed Calcination

The Waste Calcining Facility (WCF)[11] at the National Reactor Testing Station, Idaho, was designed for handling highly radioactive aluminum nitrate wastes containing relatively low concentrations of sodium. The fluid-bed calcination of some 512,000 gal of waste (radionuclide content of 20 to 40 curies/gal) was successfully carried out in the WCF[12] which was operated for 312 days with an on-stream factor greater than 99%. The feasibility of using the WCF to calcine other wastes produced at the

ICPP is being investigated in laboratory and pilot-plant studies.[13,14] Wastes being considered include aluminum nitrate wastes containing high concentrations of zirconium fluoride or sodium ion and stainless-steel wastes.

Pilot-plant work using nonradioactive aluminum nitrate waste solutions (high-zirconium fluoride or high-sodium content) is being carried out in a 12-in.-diameter fluid-bed calciner.[14] Exploratory pilot-plant tests on the calcination of zirconium fluoride–aluminum nitrate waste have been previously reported in this Review[13] and have demonstrated the following: (1) The feasibility of calcining this waste in the WCF, (2) the successful suppression of fluoride volatilization (>99% fluoride retained) by adding stoichiometric amounts of calcium nitrate to the waste solution, and (3) the negligible corrosion of austenitic type stainless steels that are used in the construction of the WCF. These exploratory tests and the fluid-bed calcination equipment used have been described in detail in a recent report by Petrie and coworkers.[15]

Calcination of high-sodium content wastes and a blend (1 to 1 by volume) of high-sodium and high-zirconium fluoride content wastes was successfully demonstrated in recently completed pilot-plant runs.[14] No caking of the bed occurred with either type of waste when the calciner bed was operated at 500°C, and the simulated wastes contained added sugar at concentrations of 2 lb/gal for the high-sodium content waste and 1 lb/gal for the blend of high-sodium and high-zirconium fluoride content wastes.

Conversion to Glasses

Work is continuing at Oak Ridge National Laboratory (ORNL) on the development of a process for the conversion of high-level-activity wastes to glasslike materials. One of the methods under investigation is a continuous melt system in which the plant waste containing glass-forming additives is fed to a horizontal, continuous melt vessel from which the melt is discharged to a final storage container.[16] This method is currently being tested in laboratory-scale and engineering-scale experiments with simulated Purex-based wastes with and without nonradioactive fission products. Two types of Purex-based wastes were used in the demonstration of the process. One of the wastes (FTW-65 X3) is a threefold-concentrated nitric acid (~1.5*M*) waste that contains sulfate ion. Prior to the concentration step, the waste is treated with formaldehyde to reduce the nitric acid concentration (to ~0.5*M*). The other waste is a sulfate-free nitric acid (3*M*) waste.

In supporting laboratory studies[17] at ORNL, various compositions of glass-forming mixes were tested for their suitability in producing glasses from these two Purex wastes in the continuous melter system. Glasses were produced which melt at 800°C and which are sufficiently fluid at 850 or 900°C to permit their use in a continuous melting process. For the FTW-65 X3 wastes, glassy products containing up to 32 wt.% waste and fission-product oxides (35,000 Mwd/metric ton equivalent) were developed from mixes utilizing varying amounts of the following fluxing additives: phosphoric acid, lithium hydroxide, sodium hydroxide, aluminum nitrate, and lead nitrate. For nonsulfate-containing Purex wastes, glassy products containing up to 22 wt.% waste and fission-product oxides (10,000 Mwd/metric ton equivalent) were developed from mixes composed of phosphoric acid and lead nitrate for fluxing additives.

As part of the overall glass fixation program, ORNL has designed a computer code for retrieving and correlating the data being generated in the development of glasses.[17] The code can accommodate all data related to the compositions, properties, and conditions of preparation of the glasses.

Laboratory-scale continuous melting experiments using simulated FTW-65 X3 wastes were made to obtain data on scale formation, volatilization of constituents, and corrosion of candidate construction materials.[17] A glass-forming melt containing the following constituents (moles per liter of waste) performed very satisfactorily whether simulated fission products were absent or present (10,000 Mwd/metric ton equivalent) in the waste feeds: phosphoric acid (3.6), sodium hydroxide (2.7), lithium hydroxide (2.4), and aluminum nitrate (0.75). The melting point and fluidity of the melt were considered suitable for use in a continuous melter. No scale was formed with this glass-producing mix.

The volatilization of constituents does not appear to be a problem, particularly if the melter off-gas is recirculated to an evaporator. Volatilization of phosphate was generally less than 0.5%, and volatilization of sulfate was

generally less than 5%. There were, however, some anomalous results with these two constituents as well as with iron and ruthenium.

Data on the corrosion resistance of the candidate construction materials were obtained at 950°C; this temperature is about 100° above the minimum temperature at which this particular melt should be sufficiently fluid for operation in the continuous melter. Of the materials tested, only platinum was unattacked. A 50% chromium–50% nickel alloy was attacked only slightly; this alloy might prove usable at a lower operating temperature. Further evaluation of these two construction materials is planned.

An engineering-scale run was conducted in a 20-in.-diameter continuous, horizontal melter constructed of type 304L stainless steel. The feed was simulated FTW-65 X3 waste containing the following fluxing additives (moles per liter of waste): phosphoric acid (1.5), lithium hydroxide (1.5), aluminum nitrate (0.5), and calcium nitrate (0.2). This glass-forming mix melts at 700 to 800°C and has an acceptable fluidity at 875°C for good melter operation. Specimens of various metals were placed in the melter to obtain information on their corrosion resistance to the vapors and melt. The metals tested included: Haynes 25, Nichrome V, Corronel 230, and types 446, 310, and 347 stainless steels.

The melter operated satisfactorily for 250 hr, at which time the run was terminated because a hole had formed in the melter as a result of corrosion. The hole was at the melt–vapor interface. Analyses of melt samples taken along the bottom of the melter showed great variations of melt composition. These variations, which cause changes in physical properties of the melt, may be detrimental to continuous melter operation.

Examination of corrosion specimens showed the following: (1) Haynes 25 and Nichrome V, some pitting attack by the vapors and little corrosive attack by the melt; (2) Corronel 230 and type 446 stainless steel, slight corrosive attack at the melt–vapor interface; (3) type 310 stainless steel, very little corrosive attack by the vapors or melt; and (4) type 347 stainless steel, completely corroded by the vapors and badly corroded by the melt.

It is planned to use type 310 stainless steel in the fabrication of the next 20-in.-diameter continuous melter.

Final Disposal Methods

Perpetual Tank Storage of High-Level-Activity Wastes

A detailed estimate of the costs of permanently storing in tanks the high-level-activity aqueous wastes that result from the processing of power-reactor fuels has been completed by ORNL.[18,19] The results of this study will serve as a basis for comparison of costs of alternative waste-management schemes.

In the study the waste-storage costs are based on the handling of the fuel from an installed reactor capacity of 70,000 Mw(t). The wastes arise from the chemical dissolution of the fuel cladding and the solvent-extraction purification of a combination of uranium and thorium converter fuels. Tank farms were designed for storage of both acid and alkaline forms of raffinate wastes from the solvent-extraction processes and of the alkaline form of the fuel-cladding wastes. The tanks are similar in design to those in use at Savannah River.[20] Tanks for containing acid raffinate wastes are fabricated of type 304L stainless steel, and those for containing alkaline raffinate wastes are constructed of carbon steel and are stress-relieved. These tanks have a storage capacity of 1×10^6 gal and are equipped with submerged cooling coils to maintain the stored wastes at temperatures not exceeding 140°F. Tanks for containing cladding wastes are also made of carbon steel and are stress-relieved. These tanks have a storage capacity of 1.2×10^6 gal and are not provided with cooling equipment.

The economics were examined for three methods of financing, these being representative of government ownership, private ownership, and a combination of government and private ownership. In each case it was assumed that, during a 20-year period of waste accumulation, a permanent fund would be established of such size that the interest would be sufficient to meet the costs of periodic tank replacement and operating expenses of the facility. (No taxes are charged either to deposits into the fund or to the interest drawn by the deposits.) Capital costs were estimated for each case and then used in a computer code to estimate total costs for each method of financing as a function of tank size, tank life, and fission-product concentration in the waste.

Total costs for storing raffinate waste, in terms of the cost of electricity generated, were least for storage of acid wastes in tanks of 75-year life with government ownership (see Fig. IV-3) and greatest for storage of alkaline wastes in tanks of 25-year life with private ownership (see Fig. IV-4). For acid wastes the optimum tank capacity is about a million gallons, and

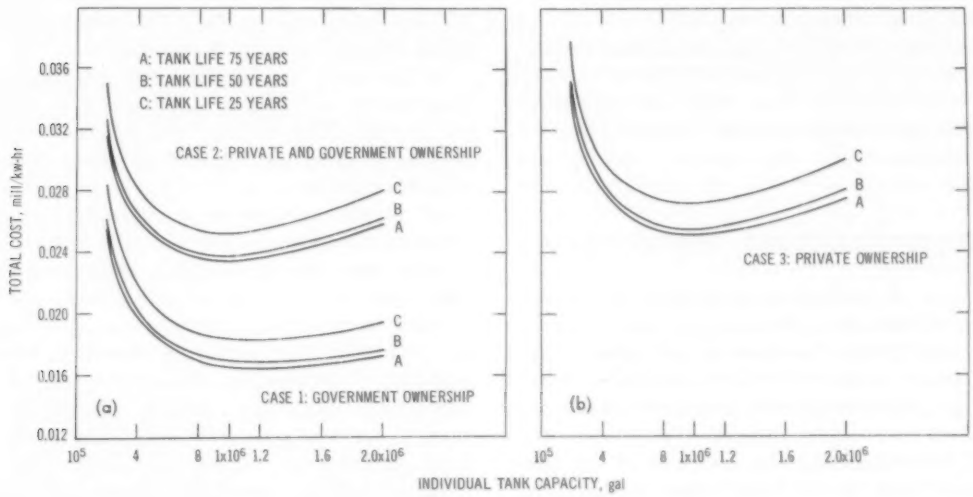


Fig. IV-3 Cost of acid-waste storage as a function of tank capacity, tank life, and method of financing for (a) *Case 1, government ownership; Case 2, private and government ownership; and* (b) *Case 3, private ownership.*[19]

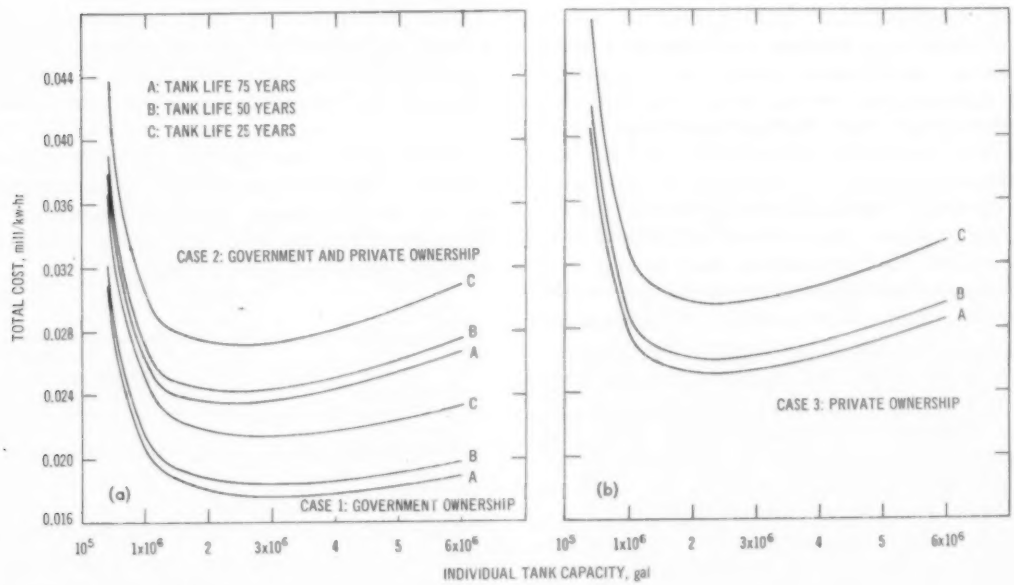


Fig. IV-4 Cost of alkaline-waste storage as a function of tank capacity, tank life, and method of financing for (a) *Case 1, government ownership; Case 2, private and government ownership; and* (b) *Case 3, private ownership.*[19]

minimum total costs range from 0.0165 to 0.0272 mill/kw-hr. For alkaline wastes the optimum tank capacity is 2.5 million gallons, and minimum total costs range from 0.0177 to 0.0294 mill/kw-hr. Doubling the concentration of fission products in the wastes, as stored, reduced the total costs between 15 and 30%.

Total costs for the storage of cladding wastes ranged from 0.0215 to 0.0398 mill/kw-hr. These costs were greater than those for raffinate storage because of the greater volumes of cladding wastes.

Fission-Product Recovery

As part of its waste-management program, PNL is developing processes for the recovery of selected fission products from Redox- and Purex-plant wastes.[21] Solvent-extraction, ion-exchange, and precipitation processes are being studied.

The Strontium Semiworks operated by the Chemical Processing Department at Hanford uses a solvent-extraction process employing D2EHPA (di-2-ethylhexyl phosphoric acid) for recovering and purifying strontium from Purex-plant acidic wastes (1WW). In the process the 1WW is first subjected to a series of precipitation, centrifugation, and dissolution steps which result in a solution that contains a concentrated, semirefined source of strontium. This solution then serves as the feed material for the solvent-extraction purification process. This flow sheet was successfully used for the previously reported[21,22] recovery and purification of about 1 megacurie of strontium needed for heat sources. Since strontium is used as a heat source, inert impurities must be kept to a minimum to maintain a high specific power and to prevent undesirable changes in the physical and chemical properties of the fuel. Magnesium, which is one of the possible impurities, has been the subject of a laboratory study by Bray[23] at PNL. Magnesium comes primarily from the uranium metal into which it is introduced by the metallurgical processes used by the uranium suppliers. Proposed changes in these metallurgical processes may significantly increase the magnesium content of the uranium metal. In the Strontium Semiworks operations, separation of magnesium from the strontium has not been a matter of concern. Currently there is very little magnesium in the uranium metal or other essential materials used. Also, in the current waste-management flow sheet, any magnesium initially present is separated from the strontium during the pretreatment (lead sulfate precipitation) of the 1WW. However, in a flow sheet that is being proposed, the lead precipitation step will not be used, and the 1WW will go directly to the solvent-extraction process.

In this study the D2EHPA solvent-extraction behavior of magnesium was found to be identical to that of strontium. The addition of complexing agents did not change their relative extractabilities.

An investigation of a precipitation process utilizing the low solubility of magnesium hydroxide was then carried out. In addition to its utility for the removal of magnesium, the hydroxide precipitation process was also studied as a method for removing other impurities (calcium, iron, cerium, and rare earths) at the same time, and thus possibly eliminating the need of the solvent-extraction process for the final purification of the strontium. For the laboratory study a simulated, semirefined strontium feed containing added radioactive tracer elements was prepared. It contained the following molar constituents: strontium (0.058), magnesium (0.017), calcium (0.012), iron (0.01), sodium (0.2), chromium (0.01), rare earths (0.002), and acid (0.12). The conditions for hydroxide precipitation were determined by heating the feed samples to 80 to 100°C and then by adjusting the *p*H to various levels with sodium hydroxide to carry out the precipitations. The resultant slurry was digested for 5 min and centrifuged. The supernatant solution was sampled for *p*H and constituent analyses. The results of the analyses of the hydroxide precipitations at different *p*H values were as follows:

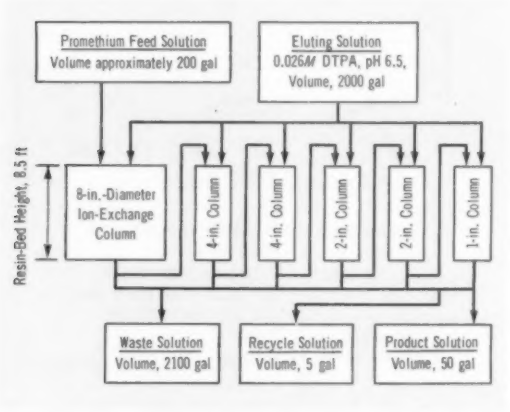
Constituent	*p*H	Percent remaining in supernatant (% originally charged)
Magnesium	10	~5
Iron and cerium	10	Essentially none
Strontium	11	~98
Strontium	13	~85
Calcium	11, 12.4, 13	~98, ~51, ~8

The results demonstrate that this precipitation process could be successfully used to purify strontium from magnesium and that it may also be applicable as the final purification step.

The final precipitate, which is somewhat gelatinous, can be separated by centrifuging. Its volume is less than 8% of the original solution. Recovery of residual strontium in the precipitate can be accomplished by washing the precipitate to dissolve the strontium which is then reprecipitated.

^{147}Pm Purification Facility at Pacific Northwest Laboratory

An ion-exchange facility for the large-scale purification of ^{147}Pm is being installed at PNL.[24] A suggested column arrangement and flow sheet[24] utilizing cation-exchange separation processes are shown in Fig. IV-5. Although a final



Run conditions
- Elution temperature, 65°C
- Elution flow rate, 4 ml/(min)(cm^2)
- Rate of band advance, 10 cm/hr

Run cycle time
- Absorption cycle, 4 hr
- Elution cycle, 180 hr
- Turn around time, 72 hr

Length of promethium band on 1-in. column, 400 cm

Pure promethium product per run, 200 g (186,000 curies)

Fig. IV-5 Promethium purification flow sheet.[24]

choice of cation resin has not been made, Dowex 50W in the hydrogen form (8 or 12% cross-linked, 50 to 100 mesh) is one of the resins being considered. An equipment capacity of 200 g (186,000 curies) of promethium per run is based on the processing of an aged feed solution* that is low in polyvalent ions but without prior removal of cerium. Preparation of a promethium of 99 to 99.5% chemical purity is planned (^{147}Pm decays to stable ^{147}Sm at a rate of 2.2%/month).

In the feed cycle the feed solution will be passed downflow through the 8-in.-diameter adsorption column until complete column breakthrough occurs, at which time the feed cycle will be terminated.

In the elution cycle the elutriant will be passed first through the 8-in.-diameter adsorption column and then in sequence through two 4-in.-diameter, two 2-in.-diameter, and one 1-in.-diameter columns. Elution will be carried out with 0.026*M* DTPA (diethylenetriaminepentaacetic acid) at *p*H 6.5.

Laboratory studies have been carried out in support of this promethium purification process.[24] Optimum-elution operating parameters for the separation of light rare earths (lanthanum through gadolinium) were experimentally determined for the eluting agents DTPA, HEDTA (hydroxyethylethylenediaminetriacetic acid), and EDTA (ethylenediaminetetraacetic acid). The recommended operating conditions were demonstrated to be as follows:

	DTPA	HEDTA	EDTA
Molar concentration	0.026	0.03–0.04	0.012
Eluant *p*H	5.5–6.5	5.0–5.5	8.4–8.6
Eluant flow rate, ml/(min)(cm^2)	4.0	4.0–5.0	3.0
Elution temperature, °C	60–70	60–70	60–70

All three eluting agents can be used in the same equipment.[24]

^{137}Cs Recovery at Pacific Northwest Laboratory

Processes are under development at PNL for the recovery of cesium from Redox- and Purex-plant alkaline supernatant solutions and Purex-plant acidic wastes (1WW).

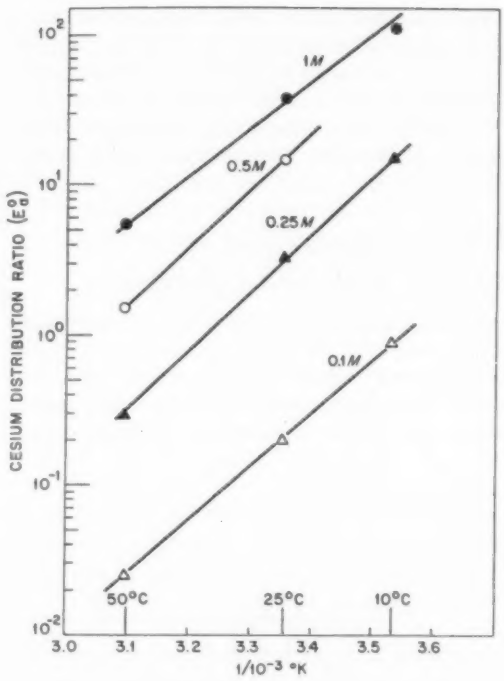
A cation-exchange flow sheet using Duolite C-3 resin was developed for recovering cesium from Redox alkaline supernatant solution.[25,26] For the loading cycle the supernatant is diluted with three parts of water and is then passed

*The feed solution is allowed to age to permit the decay removal of ^{148}Pm.

downflow through the resin column at 25°C. When the loading cycle is completed, the resin is washed with water to displace any supernatant solution remaining; the cesium is then eluted with eight column volumes of $3N$ $(NH_4)_2CO_3$ • $1N$ NH_4OH at 55°C. The elutriant contains 96 to 97% of the cesium charged in the loading cycle. For the regeneration cycle, three column volumes of $2N$ NaOH are first passed downflow through the resin column, and then four column volumes of $8N$ NaOH are recirculated through the column for 4 hr. For all cycles in the process, the solution flow rate is two column volumes per hour. This flow sheet was successfully tested with simulated and actual plant-level-activity Redox supernatant solutions.

Laboratory and pilot-plant work at PNL is being conducted to examine the possible use of a solvent-extraction process for cesium recovery from Purex-plant alkaline supernatant solution.[27,28] A solvent of interest is a high molecular weight phenol, BAMBP [4-*sec*-butyl-2(α-methylbenzyl)phenol] that was initially evaluated at ORNL.[29-31] In work with simulated wastes ($9M$ sodium, *p*H 10.3) at PNL,[27,28] BAMBP diluted with a kerosene (Soltrol-170) was found to be a very selective extractant for cesium. For maximum cesium extraction, best results were obtained[27] when the *p*H of the supernatant solution was increased from *p*H 10.3 to *p*H above 12. Cesium extraction into the kerosene-diluted BAMBP is enhanced at lower temperatures (see Fig. IV-6). This would indicate a need for temperature control for the process. If higher cesium distributions are needed, lowering the temperature may be more desirable than increasing the BAMBP concentration. The cesium distribution ratio was also found to depend on the sodium concentration in the aqueous phase, varying inversely with the aqueous sodium concentration and having a slope of slightly less than −2 over the molar sodium range of 1 to 8. Other laboratory work (see Fig. IV-7) showed that the cesium distribution ratio passes through a maximum and that the maximum shifts (from ~0.25M to 1M of additional hydroxyl ion) as the BAMBP concentration is varied from 1M to 0.1M. The sodium distribution ratios increase with increasing hydroxyl ion (the maximum sodium distribution ratios were not reached). Further work on this process is planned.

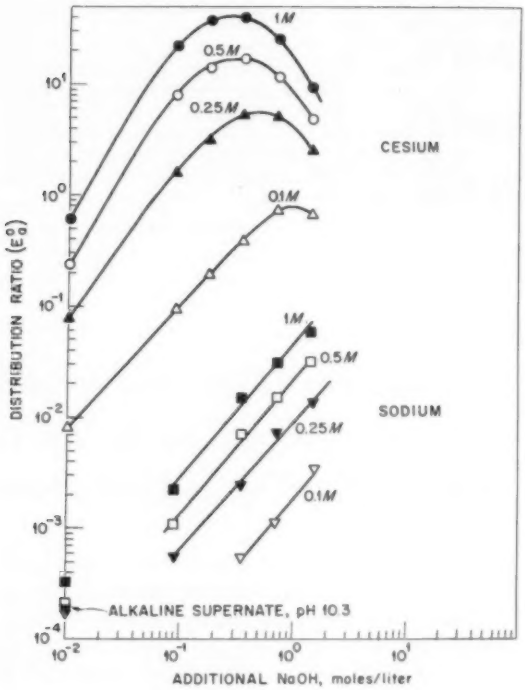
A precipitation process for removing cesium from Purex 1WW was tested on a plant scale



Organic:	BAMBP (1M − 0.1M) Soltrol-170
Aqueous:	Alkaline supernate; *p*H 10.3 (9M Na^+) plus 0.18M NaOH/liter
Temperature:	25°C
Contact time:	15 min

Fig. IV-6 Cesium distribution as a function of temperature.[27]

with full-level-activity 1WW.[32] The process involves precipitating the cesium as cesium phosphotungstate and is composed of five steps. These steps include the following: (1) precentrifugation of the Purex 1WW for the removal of precipitated fission products, (2) precipitation of the cesium by the addition of phosphotungstic acid (to a final concentration of 0.0024M) to the centrifuged 1WW and digestion for 1 hr at 25°C, (3) separation of the precipitated cesium by centrifugation, (4) washing of the precipitated cesium with 1M nitric acid for additional fission-product decontamination, and (5) dissolution of the precipitated cesium with 1M sodium hydroxide. In the plant-scale demonstration of the process, approximately 98% of the cesium was removed by a single phosphotungstic precipitation. The chemical cost of this process



Organic:	BAMBP ($1M - 0.1M$) Soltrol-170
Aqueous:	Alkaline supernate, *p*H 10.3 ($9M$ Na^+) plus indicated additional NaOH
Organic/aqueous ratio:	1
Temperature:	25°C
Contact time:	15 min

Fig. IV-7 Cesium and sodium distribution as a function of hydroxyl ion and BAMBP concentrations.[27]

was calculated to be $22 per ton of uranium processed to produce the 1WW (70 gal per ton of uranium). The phosphotungstic acid contributes 97% of the total cost.

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

By J. J. Barghusen and P. A. Nelson

Recovery of Uranium from Ores by Hydrometallurgical Techniques

The most widely used process for producing uranium concentrates is dilute aqueous leaching of the ore with sulfuric acid and, if necessary, an oxidant. The rate and degree of extraction of uranium from its ores by acid leaching depend on a number of variables: acid concentration, degree of oxidation of uranium, leaching temperature, particle size, and the extent to which the uranium minerals are locked or bound by gangue minerals. The dissolution of uranium involves several chemical reactions and is complicated by the presence of numerous impurities in the ore.

A published translation[1] gives the results of an investigation of the oxidation of UO_2 by MnO_2 in sulfuric acid solution in the presence of Fe^{2+}. It was shown that iron ions act as a catalyst during oxidation of UO_2 by MnO_2 in sulfuric acid solutions. In the presence of iron ions, oxidation of U(IV) begins at a redox potential of 350 to 400 mv which corresponds to an ion ratio of Fe(III)/Fe(II) of about 1 : 4. The rate of U(IV) oxidation increases sharply with an increase of redox potential, reaching a maximum at 550 mv. Oxidation of U(IV) at redox potentials greater than 550 mv does not increase the extent of UO_2 dissolution from uranium ore, and the maintenance of such a high redox potential during leaching leads to waste of MnO_2 oxidant.

According to Spitsyn, Nesmeyanova, and Vikulov,[2] oxidation of U(IV) is apparently effected by Fe(III) ions which in turn are reduced to Fe(II) ions and then oxidized to Fe(III) by an external oxidizing agent. The authors have observed that the oxidation of UO_2 by Fe(III) ions at *p*H of 1.5 to 2.3, with the formation of soluble UO_2^{2+}, depends on the concentration of Fe(III) and on the mixing rate and depends little on temperature in the range 20 to 60°C. The reaction in acid solution is complicated by formation of iron complexes and hydrolysis of Fe(III) ions. The oxidation of UO_2 by iron was determined to be diffusion controlled.

The effect of phosphate ions, derived from acid attack on constituents of the ore, is detrimental to the oxidation reaction.[3] The effect is not entirely due to the complexing of Fe(III) ions; the phosphate ions appear to hinder the dissolution of uranium by affecting the diffusion of reactant or product species from the mineral surface. A review of the use of various oxidants employed in the acid leaching of uranium from ores was presented in a paper by Kanevsky, Philippov, and Nesmeyanova[4] at the 1964 Geneva Conference.

Regeneration of ferric ions for oxidation of uranium ores by acid leaching can be accomplished by air oxidation of the ferrous sulfate solution in the presence of an activated-carbon catalyst.[5] The rate of oxidation of ferrous ion in sulfuric acid solutions was found to vary directly with the concentration of dissolved oxygen, the amount and specific activity of the carbon catalyst, and the concentration of ferrous ion, and inversely with the sum of the concentrations of ferrous and ferric ions.

The possibility of recovering uranium from a low-grade ore containing sulfide by high-temperature autoclave leaching in the presence

of oxygen has been reported by Nevskii, Smirnov, and Pirkovskii.[6] Oxidation of the pyrites by oxygen in an aqueous medium generates the sulfuric acid required for dissolution of the uranium. Digestion of finely divided ore for 2 hr at 140°C under 10 atm oxygen resulted in the recovery of 70% of the uranium.

Recovery and concentration of uranium from acid-sulfate leach solutions may be effected by anion-exchange techniques or by solvent extraction. Results of evaluations on the use of long-chain amines as extractants for uranium have been reported recently.[7–9] An assessment of extraction with amines as an alternative process to ion exchange for uranium recovery has indicated that the solvent-extraction route offers considerable savings over ion exchange with a reasonable return on capital investment.[8]

Production of Uranium Oxides

Production of Uranium Trioxide

One method in current practice for converting uranyl nitrate solution (UNH) to solid uranium trioxide involves spraying the solution into a heated fluidized bed of UO_3 particles. Harrell[10] has described a facility for the continuous denitration of UNH in two parallel fluid-bed reactors to produce UO_3. The design capacity of the facility is 15,000 tons of uranium per year.

The fluid-bed denitration reactor is 46 in. in diameter and 11 ft high. The fluid-bed temperature is maintained at 260 to 300°C by passing molten salt at 430°C through an array of bayonet tubes immersed in the fluidized bed. A gas mixture containing 70 vol.% steam–30 vol.% air, preheated to 540°C, serves as the fluidizing gas. The gas flow rate is sufficient to achieve a superficial velocity in the reactor of 2.25 ft/sec. Uranyl nitrate solution is introduced into the bed through a system of eight air-atomizing spray nozzles. Uranium trioxide product is continuously withdrawn from the reactor through an overflow port into a hopper. Off-gases from the reactor are filtered through a bank of 360 sintered, stainless-steel filters and then processed for recovery of nitrogen oxides and nitric acid.

Conversion of UF_6 to UO_2 and U_3O_8

A process for the direct conversion of UF_6 to UO_2 using fluidization techniques has been developed at Argonne National Laboratory (ANL). A method for producing spherical UO_2 particles of high density by reaction of UF_6 with a mixture of steam and hydrogen in a fluid bed of UO_2 particles at 650 to 700°C has been described.[11] The progress of engineering development on this process has been reported in the Summer 1965, Summer 1964, and April 1963 issues of *Reactor Fuel Processing*.[12–14]

Reese and Runion[15] have been issued a patent on a two-step process for preparing UO_2 with an average particle diameter of 0.55 to 2.5 μ from UF_6. In the initial step (see Fig. V-1) UF_6 is contacted with steam at 110 to 177°C to produce solid UO_2F_2. The product UO_2F_2 appears as a low-density powder (bulk density 0.2 g/cm^3) that tends to cling together. Since the powder does not possess a tendency to pack, the UO_2F_2 can be conveyed by a screw feeder. In the second step UO_2F_2 is reduced to UO_2 by reaction in a screw reactor (continuous calciner) with 55 vol.% H_2O–45 vol.% H_2 at 650 to 700°C for 2 hr. In a series of demonstration tests, UO_2 product with a bulk density of 0.65 to 1.5 g/cm^3 and a fluoride content of 50 to 131 ppm was produced.

It has been observed[16] that the use of an inert gas (nitrogen) in the conversion of UF_6 to UO_2F_2 (6:1 mole ratio of N_2 to UF_6) tends to promote a gas-phase reaction between UF_6 and steam, thereby giving a UO_2F_2 powder of high surface area (3 to 12 m^2/g). The recommended processing conditions include the use of 5 to 20% excess steam and a temperature of 130 to 300°C. Conversion of UO_2F_2 to UO_2 can be accomplished at 550 to 600°C by reaction with 67 vol.% H_2–33 vol.% H_2O.

Brater and Smiley[17] have estimated the capital and operating costs for plants for the conversion of UF_6 to U_3O_8 at production rates of 1, 10, and 30 tons of uranium per day. The estimates are specifically directed to the use of a UF_6 source material depleted in ^{235}U. Operating costs calculated for the conversion of UF_6 to U_3O_8 at a rate of 30 tons of uranium per day were $0.0739 per pound, which included amortization of capital at a rate of 7.7% per year. For a plant located adjacent to an established gaseous diffusion plant where credit can be given for the by-product hydrogen fluoride,

operating costs can be reduced to $0.0331 per pound.

Conversion of UF_6 to U_3O_8 is accomplished in two steps (Fig. V-2). In the first step, UF_6 is reacted with steam at 260°C in a fluid-bed reactor to form a fine, dense, free-flowing UO_2F_2 powder. The UO_2F_2 product is discharged through a rotary valve from the reactor and fed to the center of a propane–oxygen flame where, by pyrohydrolysis, it is converted to U_3O_8. Concentrated aqueous hydrogen fluoride (80% HF) is recovered by condensation from the

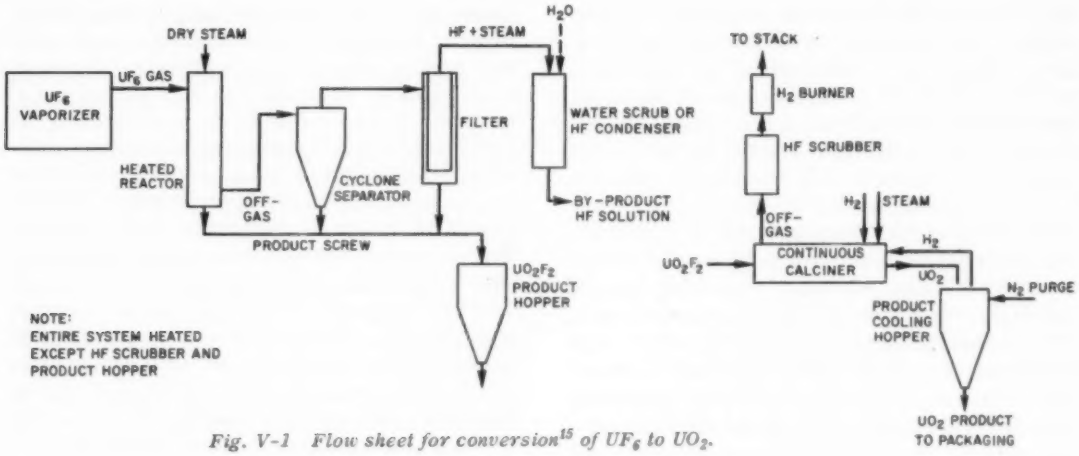

Fig. V-1 Flow sheet for conversion[15] of UF_6 to UO_2.

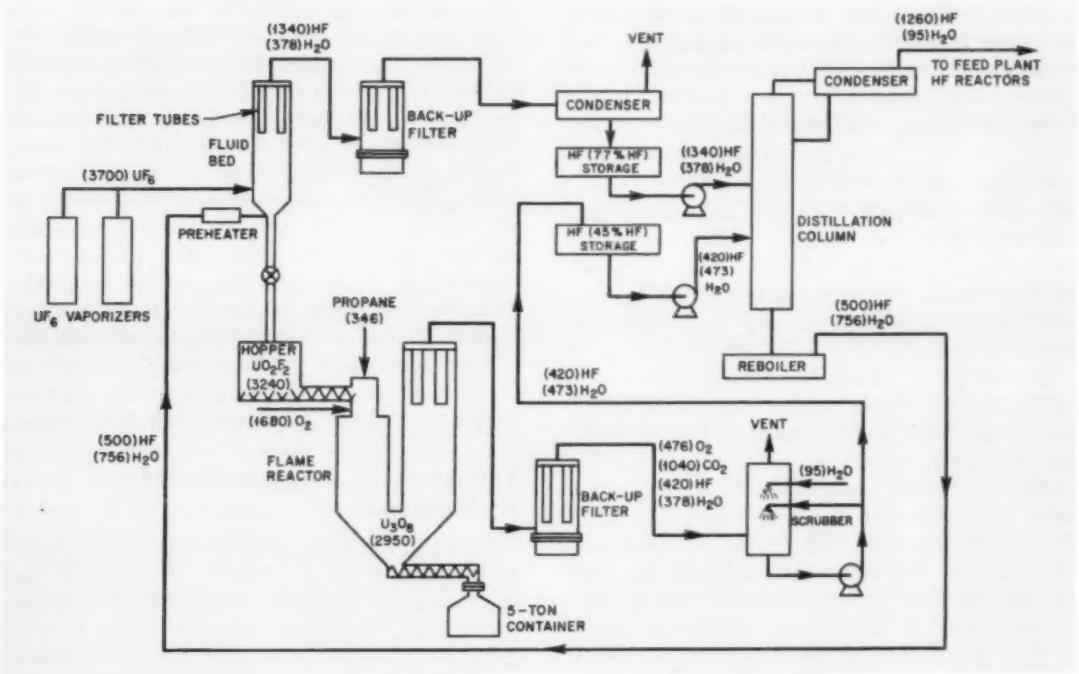

Fig. V-2 Flow sheet for conversion[17] of UF_6 to U_3O_8. (Numbers in parentheses give hourly flow rates in pounds for a plant processing 30 tons of uranium per day.)

fluid-bed reactor off-gas stream. Hydrogen fluoride is also recovered from the off-gases from the flame reactor by scrubbing with dilute hydrofluoric acid.

Reduction of Higher Oxides

The principal method for the production of UO_2 involves the reduction of higher uranium oxides, UO_3 or U_3O_8, by a gaseous reducing agent. Thus an understanding of the phase changes and kinetics of these reactions is of fundamental importance. In a study of the reduction of U_3O_8 with CO in the pressure range 29 to 200 mm, it was shown that, at temperatures above 300°C, the reaction proceeds initially at a high rate which gradually decreases to zero as oxygen is removed from the oxide.[18] The apparent activation energy was 28.6 ± 0.9 kcal/mole for U_3O_8 with a specific surface area of 2.5 m^2/g, and 18.9 ± 0.9 kcal/mole for U_3O_8 with a specific surface area of 1.1 m^2/g. The reaction rate was found to be directly proportional to the partial pressure of CO. The rate-determining stage in the reduction process was the surface reaction between sorbed CO and oxygen in the oxide. The following scheme was suggested to describe the phase transformations that accompany the reduction of U_3O_8 by CO:

$$U_3O_8 \rightarrow U_3O_{8-x_{max.}} \rightarrow \text{tetragonal phase} \rightarrow U_4O_9 \rightarrow UO_{2+x_{max.}} \rightarrow UO_{2+x}$$

Only one solid phase is presented during the reduction of U_3O_8 to $U_3O_{8-x_{max.}}$; the reaction in this stage involves the depletion of oxygen from the U_3O_8 phase. The composition of the tetragonal phase observed in this work was not precisely defined.

To provide an insight into the mechanism of reduction processes, Vlasov and associates[19] have studied the adsorption of hydrogen, carbon monoxide, ammonia, nitrogen, carbon dioxide, and water vapor on UO_3 at temperatures approximating those at which reduction of UO_3 commences. Analyses of the ammonia and nitrogen adsorption isobars indicate that the overall rate of reduction of UO_3 by NH_3 is determined by the nitrogen desorption stage. It was observed that the adsorption of gases expressed as moles per square meter increased in the following order: H_2, N_2, CO, CO_2, H_2O, NH_3.

Production of Uranium Metal

Reduction of UF_4 by Cut-Crown Magnesium

The magnesium now in use in most uranium plants as a reductant for UF_4 is obtained by chipping magnesium ingots cast from magnesium that was produced by the Pidgeon process. This process consists in the reduction of dolomite under vacuum by ferrosilicon at 1150°C and then distilling the magnesium product. The crystalline rings of magnesium obtained are termed "crowns." These crowns consist of rather loosely bound, large crystals that are relatively easy to separate by cutting. Cut-crown magnesium differs from chipped magnesium primarily in its higher specific surface area, aluminum content, and nitrogen content. If the cut-crown material can be used for uranium production, a large part of the remelting, casting, and chipping costs incurred in magnesium production can be bypassed.

Cut-crown magnesium has been evaluated at National Lead Co. of Ohio as a reductant for UF_4 in pilot-scale and production-scale tests.[20] The tests indicated that, although all reductions using cut-crown magnesium resulted in slightly poorer slag–metal separations than those obtained when reductions were made using chipped-ingot magnesium, the use of cut-crown magnesium produced generally satisfactory uranium metal. However, a detailed economic review of the quality of the UF_4 and of the uranium derbies, ingots, and fuel cores produced is required to define fully the overall cost savings resulting from the use of cut-crown magnesium. It was observed that the nitrogen and aluminum contents were uniformly higher in derbies from cut-crown magnesium than in derbies derived from chipped-ingot magnesium.

Reduction of Uranium Dioxide by Calcium

There is a considerable demand for uranium-metal powder as a primary material in the production of uranium compounds by powder metallurgy. Powdered uranium metal is frequently employed in the manufacture of uranium carbide, uranium nitride, and cermets. One process that appears promising for preparing uranium-metal powder involves the reduction

of uranium dioxide by calcium metal[21] or by calcium hydride.[22] It has been observed that the addition of 2 to 10 wt.% $CaCl_2$ to the system leads to the formation of a uranium-metal powder of larger particle size. Also, increasing the reduction temperature from 900 to 1100°C and the time of reduction from 0.5 to 4 hr promotes the formation of a product of larger particle size.[22]

Electrolytic Production and Refining of Uranium

High-quality uranium metal has been produced at the U. S. Bureau of Mines[23] by electrolytic reduction of uranium dioxide in fluoride melts at 1250 to 1300°C. A mixture of barium fluoride, lithium fluoride, and uranium fluoride was used as the electrolyte. The electrolytic cell consisted of a graphite crucible with graphite anodes and cathodes. The cell was designed such that the UO_2 was added to the electrolyte within a compartment separated from the graphite anode by a perforated barrier. Uranium metal collected as a coalesced liquid at the bottom of the cell. In general, the uranium-metal yield from the oxide feed was above 97%. Carbon was the major impurity found in the metal product; the extent of carbon contamination ranged from 100 to 2000 ppm depending on whether the metal had contacted the wall of the graphite cell. A process for producing uranium metal by electrolytic reduction of UO_2 at 1200°C in a fused salt containing BaF_2, MgF_2, and UF_4 has been described.[24]

Sullivan and associates[25,26] at the U. S. Bureau of Mines have developed a method for electrorefining magnesium-reduced uranium in molten-chloride electrolytes. Three electrolyte systems were evaluated: $LiCl-KCl-UCl_3$, $NaCl-KCl-UCl_3$, and $NaCl-UCl_3$. The construction of the electrolytic cells varied with the electrolyte composition: a mild-steel container with a molybdenum liner to prevent contact of the uranium anode with the steel was used with the $LiCl-KCl-UCl_3$ electrolyte; a Hastelloy C cell completely lined with molybdenum sheet was employed with the $NaCl-KCl-UCl_3$ system; for tests with $NaCl-UCl_3$, the cell was a tantalum crucible fabricated from 14-gauge plate. The method for adding UCl_3 to the alkali chlorides involved the formation of UCl_3 by reaction between uranium metal and hydrogen chloride within the molten electrolyte. Molybdenum was found to be the most satisfactory cathode material.

The refined uranium deposit appeared as crystals and dendrites on the cathode. On conclusion of the electrodeposition, the cathode deposit was withdrawn from the electrolyte and suspended above the surface of the melt to allow most of the entrained salt to drain from the metal crystals. The deposit was leached in portions of dilute acetic acid solution until a chloride-free solution was obtained. The crystals were then washed with distilled water, rinsed with acetone, and dried. The refined uranium was stored under an argon atmosphere.

It was found that uranium can be electrorefined to a high degree of purity in all three electrolyte systems studied. The following conditions were established[25] for operating the cell with the ternary electrolyte systems: cell voltage, 0.20 to 0.60 volt; initial cathode current density, 200 to 1500 amp/sq ft; uranium concentration in the electrolyte, 7 to 10 wt.%; electrolyte temperature, 500 ± 50°C for the $LiCl-KCl-UCl_3$ system, and 850°C for the $NaCl-KCl-UCl_3$ system. It was necessary to operate the cell at a temperature 100 to 200°C above the melting point of the electrolyte to avoid a seeming depletion of the uranium content in the electrolyte caused by low mobility of the uranium ions in the melt. This seeming depletion was eliminated by raising the electrolyte temperature.

The operating conditions established[26] for the $NaCl-UCl_3$ system were: cell voltage, 0.2 to 0.8 volt; initial cathode current density, 300 to 1500 amp/sq ft; uranium concentration in the electrolyte, 8.7 to 13.3 wt.%; electrolyte temperature, 860°C. The concentration of alkali metals in the washed uranium crystals usually was approximately 100 ppm, but after consolidation of the refined uranium by arc melting, the alkali-metal content in the metal was reduced to 5 ppm.

In other work, Smirnov and associates[27–29] have investigated electrolytic processes and the electrochemical behavior of uranium in fused $NaCl-KCl$. In a study of the cathode polarization of molybdenum electrodes in $NaCl-KCl-UCl_3$ melts containing 0.5 to 12.0 wt.% uranium at 690 to 900°C, it was confirmed that metallic uranium is deposited on the cathode by virtue of the primary discharge of U^{3+} ions.[29] In melts containing UCl_4, deposition of

metallic uranium on the cathode is preceded by residual currents connected with the reduction of U^{4+} to U^{3+} ions and also with the reduction of UO_2^{2+}, which forms readily as a result of reaction of the electrolyte with oxygen, even in trace amounts.[29]

Preparation and Properties of Plutonium Dioxide

The standard feed for the production of PuO_2 or mixed (U, Pu)O_2 is a dilute solution of plutonium or uranium–plutonium in nitric acid. Preparation of (U, Pu)O_2 involves coprecipitation of ammonium diuranate–plutonium hydroxide by addition of NH_3 to the nitrate solution and drying of the precipitate, followed by calcination in 6 vol.% H_2–94 vol.% N_2 at 840°C for 3 hr. Roth and Halteman[30] have performed microscopic examinations of (U, Pu)O_2 materials over the entire composition range and of the precursors from ammonium diuranate–plutonium hydroxide coprecipitation. The examinations showed that the morphological characteristics of the (U, Pu)O_2 powders are determined by the initial precipitation chemistry and thereafter are transferred from step to step throughout the oxide-preparation process.

In a study of the physical and chemical properties of PuO_2, Moseley and Wing[31] prepared PuO_2 by calcination of plutonium oxalate, nitrate, hydroxide, and peroxide at temperature levels of 240, 400, 600, 500, and 1000°C. Plutonium dioxide derived from plutonium peroxide was of higher density than PuO_2 derived from the other precursors. In general, the density and crystallite size of PuO_2 increased as the calcination temperature was increased. Specific surface area of the PuO_2 decreased in the following order: oxalate, hydroxide, nitrate, peroxide.

Sinterability of PuO_2 powders prepared by calcination of plutonium oxalate, hydroxide, and peroxide has been evaluated in a series of performance tests.[32] The feed powders were compacted at 10 to 40 tsi without binder, and the compacts were sintered at 1600°C in molybdenum boats under flowing 6 vol.% H_2–94 vol.% N_2 or in platinum boats under flowing oxygen. Generally, higher densities resulted from compacts sintered in oxygen since sintering in a reducing atmosphere tends to induce the formation of lower density suboxides. Plutonium dioxide prepared by precipitation of Pu(IV) oxalate followed by calcination was the most sinterable powder (see Table V-1). The

Table V-1 SINTERING CHARACTERISTICS[32] OF PuO_2
(Sintered at 1600°C for 1 hr in N_2–6% H_2 or in O_2)

Powder preparation route	Batch designation	Compaction pressure, tsi	Green density, g/cm³	Fired density, g/cm³		Fired density, % of theoretical PuO_2	
				N_2–6% H_2	O_2	N_2–6% H_2	O_2
Oxalate	Pu4-4	38	6.36	10.34	10.94	90.4	95.6
	Pu5-2	38	5.85	10.35	10.90	90.5	95.2
	Pu9-3	38	7.51	10.33	10.60	90.1	92.6
	Pu38	40	7.25	9.58	10.55	83.6	92.1
	Pu27	10	6.50	9.93	10.49	86.6	91.5
	Pu27	20	7.01	10.21	10.70	89.1	93.4
Hydroxide	78-38-A	32	8.08	9.94	9.92	86.7	86.6
	78-38-B	32	5.95	10.34	10.71	90.2	93.5
	17-8-A	32	7.81	9.50	9.57	82.9	83.5
	17-8-B	32	6.90	9.70	9.85	84.6	85.9
	78-46-A	32	5.75	10.36	10.35	90.4	90.3
Peroxide	Pu29	20	6.60	9.24	9.45	80.6	82.5
	Pu29	40	7.04	9.26	9.87	80.8	86.1
	Pu30	20	6.20	9.75	10.07	85.1	87.9
	Pu30	40	6.73	10.28	10.51	89.7	91.7
	Pu31	20	7.10	10.21	10.49	89.1	91.5
	Pu31	40	7.57	10.12	10.71	88.3	93.4
Denitration		12	6.85	9.32	10.30	81.3	89.9
Metal oxidation—air	Pu59A	40	8.87	9.05	9.04	79.0	78.9
Metal oxidation—steam	Pu59B	40	7.88	9.64	9.09	84.0	79.4

microstructure of PuO_2 compacts sintered in a reducing atmosphere was quite variable, and the texture was more dependent on the precipitation process than on the sintering conditions.[32]

Reference 33 presents the results of a study on the sintering behavior of (U, Pu)O_2 mixtures. Pellets having 96 to 99% of the theoretical density were prepared by sintering (U, Pu)O_2 containing 20 wt.% PuO_2 for 4 hr at 1650°C in flowing hydrogen.

Production and Purification of Plutonium Metal

Plutonium metal is generally prepared by the reduction of plutonium fluoride with calcium metal in an inductively heated pressure vessel. A savings in process costs might be realized if plutonium could be prepared by the direct reduction of plutonium dioxide since this route would obviate the costly preparation of plutonium fluoride. For the production of ^{238}Pu metal, an oxide route would reduce significantly the neutron radiation that arises from the (α,n) reaction with fluorine. A series of tests was performed to evaluate the reduction of PuO_2 by calcium metal.[34] Fluxing agents consisting of fluoride salts or mixed chloride and fluoride salts were added to dissolve the CaO product and to assist in the production of a coalesced metal product. Although finely divided metal was produced, the metal coalesced only with the chloride–fluoride flux, and then in small yield (2%).

Fused-salt electrorefining processes have been developed at Los Alamos Scientific Laboratory for producing high-purity plutonium metal in an electrorefining plant at the rate of 40 kg/month.[35] Impure plutonium metal, plutonium–10 at.% iron alloy and plutonium–3 at.% gallium alloy, has been refined routinely to plutonium containing less than 100 ppm metallic impurities by weight. In addition to serving as a means of preparing high-purity plutonium metal, the refining facility is used to recycle plutonium-metal scrap economically. A complete description of the electrorefining equipment and procedure was reported in the October 1962 issue of *Reactor Fuel Processing*.[36] At the present state of development, three metallic impurities, iron, americium, and tungsten, are routinely detectable in electrorefined plutonium. The major impurity, tungsten, comes from the use of tungsten cathodes in the refining process. Incorporating the use of a carburized tantalum cathode (a tantalum cathode that was heated in hydrogen to 1700°C in the presence of carbon to produce a TaC phase on the surface) significantly reduced the level of metallic impurities in the refined metal.[37] The concentration of tungsten was reduced to less than 2.5 ppm. It was observed, however, that the concentration of carbon in the metal increases slightly upon reuse of the cathode. Other methods under development for producing plutonium metal of high purity include electrolysis of the solid metal[38] and zone melting.[39]

Production and Properties of Uranium and Plutonium Carbides

Increasing consideration is being given to the production of (U,Pu)C and to the coupling of the production of (U,Pu)C with carbide fuel reprocessing. Methods of preparation are reviewed in recent papers,[40–42] and physical, mechanical, chemical, and compatibility properties of uranium carbides are described.[40,42] A bibliography[43] on uranium carbides, nitrides, and silicides contains 790 references, most of which include abstracts on the preparation and properties of these materials.

Carbothermic Reduction Method

The carbothermic reduction method for the preparation of UC from UO_2 and from U_3O_8 and for the preparation of UC_2 from UO_2 has been studied by Yamamoto.[44] The UO_2 and U_3O_8 powders with natural graphite powder were mixed by ball-milling for 6 hr, sieved, and compressed at 1 torr/cm^2 into 10-mm-diameter by 10-mm-long cylindrical pellets. The pellets were fired at 1000°C to 2000°C for 1 hr in a graphite resistance furnace under a vacuum of 10^{-3} to 10^{-4} torr. In the preparation of UC from UO_2, the reaction $UO_2 + 3C \rightarrow UC + 2CO$ was complete within 1 hr at 1500°C with

no free carbon detected and only the UC phase appearing in X-ray diffraction analyses.

Free carbon remained in amounts of 1 to 2% in attempts to make UC_2 by the reaction $UO_2 + 4C \rightarrow UC_2 + 2CO$. When the carbon content was varied, free carbon was found to be present only at carbon-to-uranium ratios greater than 1.86. However, even at higher values of the ratio, UC was also present, as indicated by X-ray diffraction analysis and microstructure examination. It was concluded that the amount of carbon in "UC_2" phase of the conventional tetragonal crystal system would be greater than that in $UC_{1.86}$, which is the commonly accepted composition.[42]

In attempting to make UC from U_3O_8 by the reaction $U_3O_8 + 11C \rightarrow 3UC + 8CO$, Yamamoto found that a considerable amount of CO_2 was evolved at about 800°C. This was confirmed by Strausberg at Atomics International[45] who studied the reaction in greater detail. It was shown by Strausberg that the carbothermic reduction of U_3O_8 to UC can be done in two steps by the reactions: first, $U_3O_8 + C \rightarrow 3UO_2 + CO_2$ (800 to 900°C) and, second, $UO_2 + 3C \rightarrow UC + 2CO$ (>1300°C). The overall reaction is: $U_3O_8 + 10C \rightarrow 3UC + 6CO + CO_2$. Verification of the first step was achieved in runs in which the CO and CO_2 given off at temperatures below 800°C were collected and measured. The overall reaction was tested in runs in which agglomerates of U_3O_8 and carbon, held together with polyvinyl alcohol (PVA) binder, were reacted at 1700 to 2000°C. The oxygen concentrations in hyperstoichiometric carbide products UC_{1+x} (300 to 400 ppm oxygen) were lower than in hypostoichiometric carbide products (500 to 1000 ppm oxygen) in small-scale runs. The results for two multikilogram runs are shown in Table V-2.

Other Methods of Synthesis

The work at ANL on preparation of UC and (U,Pu)C by a liquid-metal process, a molten-salt process, and a fluid-bed process was discussed in the Fall 1965 issue of *Reactor Fuel Processing*.[46] Additional data on these methods are given in Ref. 47.

Three other methods of preparing mixed (U,Pu)C are being studied by Tope and Talaber at Argonne:[48]

$$U_x - Pu_y + C \rightarrow (U_xPu_y)C \quad (1)$$

$$xUC + yPuC \rightarrow (U_xPu_y)C \quad (2)$$

$$(x-y)\ UC + xUC_2 + yPu \rightarrow (U_xPu_y)C \quad (3)$$

In a test of the first method, uranium–20 wt.% plutonium alloy was vacuum melted in a graphite crucible. The results were not encouraging in that the maximum carburization obtained at 2000°C was only 3.8 wt.% carbon. The reaction rate for the alloy was much lower than had been obtained in previous experiments with pure plutonium. It should be noted, however, that reaction 1 has been successfully carried out in the past[49] and recently[50] by the arc melting of plutonium–uranium alloys in contact with carbon in a water-cooled copper crucible. Reaction 2, carried out with fused carbides, resulted in some regions of unreacted UC when 177-μ particles were employed. Two heating cycles with an intermediate grinding step are believed to be necessary to obtain complete solid solution. Experimental work on reaction 3 is just beginning.

Sintering and Chemical Properties

Plutonium monocarbide pellets having 93% of the theoretical density were pressed and sintered from powder prepared by crushing arc-melted buttons.[51] Powders with particle sizes of less than 74, less than 44, and less than 15 μ had optimum sintering temperatures of 1400, 1350, and 1250°C, respectively. The weight losses were quite high, being about 3 and 7 wt.% after 2 hr of sintering at 1400 and 1500°C, respec-

Table V-2 CARBOTHERMIC REDUCTION[45] OF U_3O_8 TO UC_{1-x}
(Reacted for 2 to 3 hr at 850 to 900°C and then for 4 hr at 2000°C)

Charge weight, kg	U_3O_8 analyzed		Charge ratio, atoms of C/mole of U_3O_8		As-sintered UC			
	U, %	N_2, ppm	From PVA	Total	Carbon content, % Calculated	Carbon content, % Analyzed	Oxygen, ppm	Nitrogen, ppm
16		30	0.42	9.94	4.68	4.74 ± 0.04	1120 ± 235	480 ± 150
20	84.3		0.42	9.93	4.66	4.62 ± 0.04	1640 ± 400	400 ± 60

tively. Weight loss due to vaporization at high temperatures was accompanied by an increase in carbon concentration. This result is in agreement with the volatility studies of Potter,[52] which indicated that considerable decomposition of PuC takes place at 1550°C and is accompanied by plutonium vaporization. The melting point of the sintered PuC pellets in the studies by Kruger[51] was determined to be 1663 ± 10°C.

The reduction of hyperstoichiometric UC and (U,Pu)C powder pellets was studied at Harwell.[53] Reduction with hydrogen of hyperstoichiometric powders of UC and (U,Pu)C (1 to 2 m^2/g surface and up to 5.6 wt.% carbon) was rapid at the optimum temperature of 850°C, and was completed (reduction to UC, 4.8 wt.% carbon) in 2 hr or less. Above temperatures of 1100°C the reaction rate was very low because of the low equilibrium pressure of the reaction product methane. Reaction of hydrogen with hyperstoichiometric UC pellets during sintering also successfully removed excess carbon. A quantity of green pellets containing 4 to 5 g of hyperstoichiometric UC (5.6 wt.% carbon) and 2 wt.% nickel sintering aid were reduced to stoichiometric pellets in a sintering cycle that consisted of increasing the temperature at a rate of 640°C per hour, holding the pellets for 1 hr at 1500°C, and then decreasing the temperature at an initial rate of about 700°C per hour. A heating rate of 900°C per hour resulted in residual excess carbon. Hyperstoichiometric pellets of $(U_{0.85}Pu_{0.15})C$ measuring 7 mm in diameter by 4 mm and containing 5.3 wt.% carbon were sintered to high densities in a hydrogen atmosphere, but 15 to 30% of the excess carbon was retained in the central core region of the pellet even when slow heating was employed. Dilution of the hydrogen with inert gas resulted in a decrease in the rate of reduction.

The effect of phase dispersion on the hydrolysis of uranium monocarbide–dicarbide mixtures was studied in experiments in which the relative amounts of hydrogen and hydrocarbon gases given off on hydrolysis were measured.[54] The deviation of the relative concentrations of hydrocarbon products from the values calculated for mixtures of the monocarbide and dicarbide is a function of the degree of dispersion of the phases; with good dispersion of phases, such as in as-cast mixtures, maximum deviations were observed.

Carbide Fuel Cycles

Of the three major fast breeder reactor fuels, the fuel cycle cost for (U,Pu)C fuel may prove to be lower than that of either of the other two fuels, namely, metal and oxide.[40,41,55] Moreover, greater emphasis is now being given to the combining of fuel processing, fuel synthesis, and fuel fabrication into an integrated cycle for carbide fuel. Several alternatives for such a cycle are illustrated in Fig. V-3 (next page), which is from the report by Wheelock.[41]

Preparation of Uranium and Plutonium Nitrides

Discussions of the preparation of UN by direct reaction of nitrogen with uranium powder formed by hydriding and dehydriding bulk uranium were given in the Winter 1964–1965 issue of *Reactor Fuel Processing*.[56] Preparation of UN by this method results in a powdered product of fairly low bulk density of 3 to 7 g/cm^3 because of the formation and subsequent vacuum decomposition of higher nitrides. A method is being studied at Argonne which produces a product with a high bulk density.[57] In this study UN is prepared by reaction of nitrogen with uranium turnings or uranium shot in a heating cycle that prevents formation of significant amounts of higher nitrides. In an experiment with 90 g of uranium turnings, 40% of the nitrogen required for conversion to UN was reacted at temperatures below 1100°C. The final reaction temperature was 1300°C; at this temperature the reaction was complete after 20 min. The nitride coating on the turnings contained the molten uranium (m.p. 1132°C) during the last step of this process. The pressure was reduced from 200 torrs to 5×10^{-5} torr in a period of 15 min with no evidence of nitrogen evolution from the reaction product. The product, which was still in the form of the original turnings, was ground into a coarse powder having a bulk density of 8.0 g/cm^3. The nitrogen content of the ground product was 5.6%. Similar results were obtained when uranium shot of 0.71- to 1.41-mm diameter was nitrided.

High-density UN was prepared at Battelle Memorial Institute[58] by inert-electrode arc melting and by consumable-electrode arc melting. Table V-3 summarizes results for arc melting of 75-g buttons of uranium with a

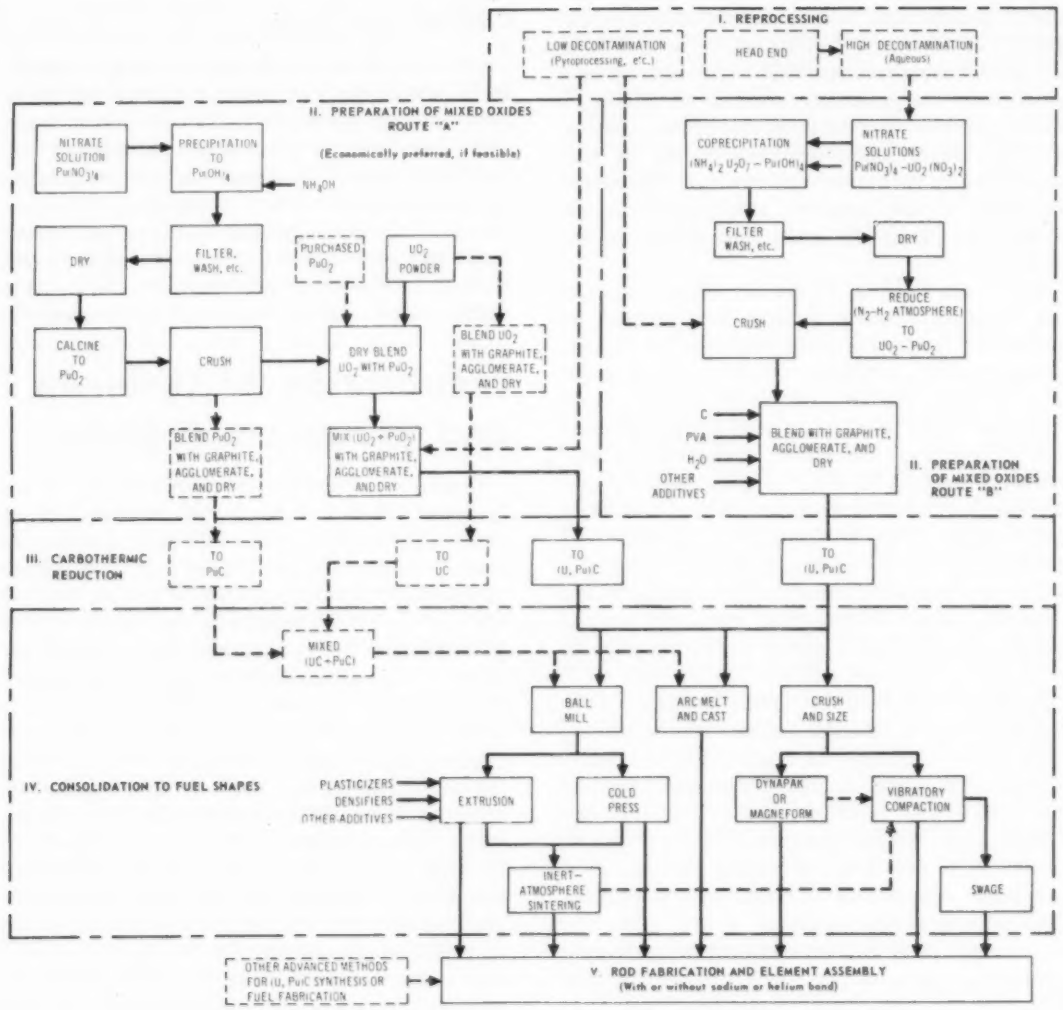

Fig. V-3 Mixed carbide fuel-cycle alternates.[41]

tungsten electrode. The best nitrogen pressure for producing stoichiometric UN was found to be about 240 psig. The effect of hydrogen in the gas atmosphere appeared to be merely that of increasing the total pressure. Both polycrystalline UN and large single crystals of UN were prepared by the consumable-electrode method. The technique employed a $\frac{1}{4}$-in.-diameter uranium electrode that was reacted inside a 1-in.-diameter by $1\frac{1}{2}$-in.-deep water-cooled copper crucible. The electrodes were pretreated for 5 min at 100 amp and 100 volts and then melted at 140 amp and 100 volts under an initial nitrogen pressure of 20 atm. Polycrystalline UN castings, 1 in. in diameter by $\frac{1}{2}$ in. long, with a nitrogen content varying from 5.5 to 6.0 wt.%, were obtained by this method. Large (>1 cm^3) single crystals were formed by using a preformed UN ingot section in the copper crucible and carrying out the runs at a very low rate and under slightly excessive nitrogen pressures. Some properties of cast UN, which were determined with the above materials, are the following: hardness at room temperature and at 800 to 1400°C and thermal and electrical conductivity.

Table V-3 NITRIDATION OF URANIUM BY ARC MELTING IN NITROGEN WITH A TUNGSTEN ELECTRODE[58]

Melt*	Absolute pressure, atm: Hydrogen	Absolute pressure, atm: Total	Absolute pressure, atm: Average total during melting	Arc length, in.	Change in weight of tungsten tip, g	Button analysis: N_2,† wt.%	Button analysis: O_2, ppm	Button analysis: H_2, ppm	Button analysis: W, wt.%
1	⅓	10⅓	14	0.16–0.44	−0.03	5.61			0.10
2	⅓	14⅓	20	0.5–0.6	+0.68	6.01	68	2	0.25
3	⅓	19⅓	26	0.25–0.31	+0.01	5.94	65	1.7	0.11
4	0	10⅓	15	0.91–0.94	+0.34	5.78			0.07
5	0	14⅓	20	0.31–0.56	+1.09	6.03	93	3.6	0.07
6	0	19⅓	28	0.09–0.19	+2.68	6.85	63	1.9	0.27

*Each 75-g uranium button was melted for 5 min per side.
†Kjeldahl method.

Preparation of PuN by carbon reduction of PuO_2 under 600 mm of nitrogen was reported by Carroll.[59] The reaction proceeds as follows:

$$PuO_2 + 2C \xrightarrow[N_2]{1600°C} PuN + 2CO$$

X-ray diffraction analyses showed a single phase having a cubic structure with a lattice parameter of 4.907 ± 0.001 A, which is slightly larger than the commonly accepted value of 4.906 ± 0.001 A. This may have been caused by residual carbon which was determined to be 1120 ppm.

Phase studies and studies of the thermodynamic, oxidation, and corrosion properties of the uranium–nitrogen system are reported by Bugl and Bauer.[60] The pressure–temperature dependence of UN decomposition and melting, of equilibrium between the UN and U_2N_3 phases, and of nitrogen solution in the U_2N_3 phase was determined as well as the solubility of UN in liquid uranium. Thermodynamic functions were calculated from these data. The oxidation kinetics of UN in CO_2, oxygen, and water-saturated air were found to obey the linear rate law with activation energies ranging from 10,400 to 15,400 cal/mole.

Preparation of Uranium and Plutonium Sulfides

Uranium monosulfide is usually prepared by a gas–metal reaction described in the Winter 1964–1965 issue of *Reactor Fuel Processing*.[61] Attempts to prepare US by two fused-salt processes were unsuccessful.[62,63] In the first process attempted, an H_2–H_2S gas mixture was bubbled through molten alkali halides containing UF_4. Mixtures of UOS and UO_2 were obtained as products, rather than US, when the salts were not dried. A product was not obtained with dried salts in runs conducted at temperatures up to 750°C. In the second process UF_4 or UCl_4 and either dried Na_2S or CaS were dissolved in an alkali chloride solution which was electrolyzed. Under the driest conditions, UOS was obtained.

Kruger and Moser[63] prepared PuS by reacting partially decomposed plutonium hydride with hydrogen sulfide in the temperature range 400 to 600°C followed by homogenization for 4 hr under vacuum at 1500 to 1600°C. The product contained about 0.01 wt.% oxygen and 0.01 wt.% nitrogen. The lattice constant determined for this material varied from 5.5383 ± 0.0001 to 5.5409 ± 0.0001 A. The sintering characteristics of PuS were determined. Powdered PuS (< 44 μ) was mixed with 0.5 wt.% Carbowax binder, pressed at 2110 kg/cm², and sintered at 1500 to 1900°C. Pellets sintered in vacuum at the optimum temperature of 1600°C attained a density of 94% of theoretical with a weight loss of 1.2 wt.% that included the 0.5 wt.% loss resulting from the evaporation of the binder. Under flowing argon the maximum density, 92% of theoretical, was obtained at 1700°C. The electrical resistivity of PuS at room temperature was determined to be 2450 ± 150 μohm-cm. The average linear thermal-expansion coefficient for the temperature range 18 to 960°C was 18.54×10^{-6} per degree centigrade.

The uranium–US phase diagram is being studied at Argonne.[64,65] Uranium metal was equilibrated with a uranium monosulfide crucible. Compositions of the quenched liquid phase were determined by chemical analysis. A tentative phase diagram is given in Fig. V-4.

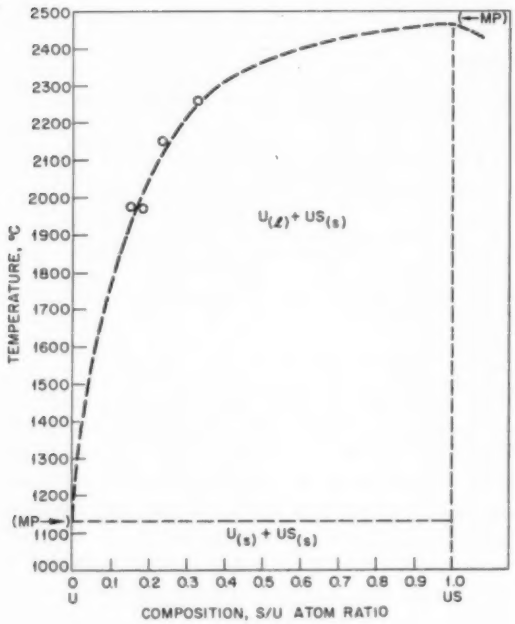

Fig. V-4 Tentative phase diagram for the uranium–uranium monosulfide system.[64]

Preparation of Uranium and Plutonium Phosphides

Preparation of UP by reacting finely divided uranium with phosphine gas (PH_3) was studied by Baskin and Shalek.[66] Uranium powder was formed by hydriding uranium turnings and decomposing the hydride; this treatment was followed by two more such cycles to obtain a very fine powder. Measured amounts of phosphine were reacted with the uranium at 280 to 720°C to produce products with plutonium-to-uranium ratios in the range 0.98 to 1.30, as determined by weight gain. The products were fired in a tungsten crucible at 1400°C for 2 hr with the pressure never exceeding 8×10^{-5} torr. The fired material contained small amounts of unreacted uranium that were removed by screening out the +200-mesh size fraction. The products of nine runs contained 0.18 to 0.29 wt.% oxygen and 11.20 to 11.43 wt.% phosphorus as compared with the theoretical phosphorus content for UP of 11.51 wt.%.

Pellets of UP were prepared and fired for 1 hr in vacuum in experiments by Baskin and Dusek.[67] The density of pellets prepared from powder that was ball-milled for 5 hr ranged from 93.7% of theoretical at 1600°C to 96.7% at 2200°C. Pressing and sintering of powder that was not ball-milled yielded pellets having densities of 86.8 to 96.1% of theoretical when fired at the respective temperatures given above.

Baskin[67,68] also studied the oxidation behavior of UP. Uranium monophosphide exhibited greater oxidation resistance than the compounds UC, UN, US, and UAs. After maintaining the fine powder at 190 to 210°C in static air for 270 hr, the weight gain was only 1.87%. This oxidation resistance was attributed to the formation on the surface of an amorphous phase containing P_2O_5 and UO_2.

Kruger and Moser[69] prepared PuP by the phosphine–metal reaction and also by reaction of the elements in a pressure vessel. In preparation by the gas–metal reaction, the purest product contained 0.052 wt.% oxygen and 0.067 wt.% nitrogen. In the second method plutonium powder was prepared by hydriding bulk plutonium at 200°C and dehydriding at 600°C, followed by grinding to a particle size of less than 44 μ. The plutonium powder and red phosphorus powder were then mixed and reacted for 5 hr at 550 to 650°C. Excess phosphorus was separated from the PuP by evaporation. X-ray analysis indicated single-phase PuP, and chemical analyses showed the product to contain 0.15 wt.% oxygen and 0.02 wt.% nitrogen. This product was crushed to less than 44-μ powder, which was then mixed with 0.5 wt.% Carbowax binder, pressed at 2110 kg/cm², and sintered at less than 5×10^{-5} torr pressure for 2 hr at 1400 to 1750°C. A maximum density of 88% of theoretical was achieved at a sintering temperature of 1600°C with a weight loss of 2.1%. The melting point was determined to be approximately 2900°C.

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